Tetrahedron Letters, Vol. 22, No. 16, pp 1495 - 1496, 1981
Printed in Great Britain

0040-4039/81/161495-02$02.00/0

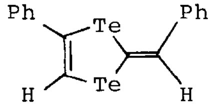
SYNTHESIS OF *cis*- and *trans*-2,4-DIBENZYLIDINE-1,3-DITELLURETAN FROM SODIUM PHENYL ACETYLIDE AND TELLURIUM METAL; A REINVESTIGATION AND STRUCTURE PROOF

Steven L. Bender, Neil F. Haley, and Henry R. Luss
Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650

Summary: Reaction of sodium phenyl acetylide with tellurium metal and subsequent protonation yields the title compounds, rather than a 1,3-ditellurole as recently reported.

Our interest in tellurium analogs of 1,3-dithiols prompted us to repeat the recently reported Russian synthesis of 1, to our knowledge the only 1,3-ditellurole appearing in the literature.[1] The reported synthesis of 1, utilizing a minor variation[2] of the procedure used to prepare the corresponding 1,3-dithiole and diselenole,[3] is shown in eqn. (1).

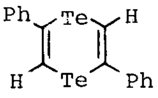
$$Ph\text{-}C{\equiv}C^{\ominus}Na^{\oplus} + Te \xrightarrow{DMSO/Et_2O} [Ph\text{-}C{\equiv}C\text{-}Te^{\ominus}Na^{\oplus}] \xrightarrow{HCl/Et_2O}$$



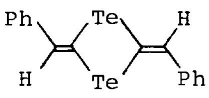
1

(1)

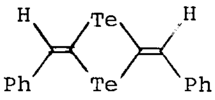
Our use of the Russian procedure yielded a product corresponding to 1 in m.p. (270-275°C, from chlorobenzene), in crystal form and color (orange-red platelets), and in solubility,[4] but we could not obtain the reported NMR spectrum.[5] The low solubility of our product limited the NMR solvent choices to deuterated hexamethylphosphoramide (HMPA). The pulsed Fourier transform 270 MHz NMR spectrum in HMPA shows a classic monosubstituted phenyl splitting pattern[6] along with a singlet at δ 8.60 ppm (TMS as internal standard) which integrated for one proton per phenyl group. The field-desorption mass spectrum supported the dimeric molecular formula of $C_{16}H_{12}Te_2$ with a molecular ion at m/e = 464 (Te^{130}) having the expected isotope pattern for Te_2. The elemental analysis also supports this empirical formula. This information suggested symmetrical dimeric structures such as the 1,4-ditellurin 2 or the geometric 1,3-ditelluretan isomers 3 and 4.



2



3



4

We also isolated a lower-melting second product from the filtrate (reddish needles, m.p. 175-177°C, from chloroform/heptane) whose NMR spectrum (HMPA with TMS) again shows a classic monosubstituted phenyl pattern and a singlet at δ 8.51 ppm.

NOTE: Future correspondence should go to Dr. Haley.

The FD mass spectrum also shows a m/e = 464 molecular ion and an isotope pattern for Te_2. This lower-melting compound was converted to the higher-melting isomer by irradiation or acid catalysis.

The structures of the above materials were determined from a single-crystal X-ray analysis of the higher-melting compound.[7] The compound was shown to be the *trans* isomer 3, a 2,4-dibenzylidine-1,3-ditelluretan (Fig. 1) and not a 1,3-ditellurole as expected from Ref. 1. The analysis revealed a close intramolecular Te-H distance (2.69 Å) and an intermolecular Te-Te distance [3.630(1) Å] which is significantly less than the sum of their van der Waals radii (4.40 Å).[10] By analogy, the lower-melting compound is assigned structure 4, the *cis* isomer of 3. To our knowledge, this is the first report of a 1,3-ditelluretan ring system.

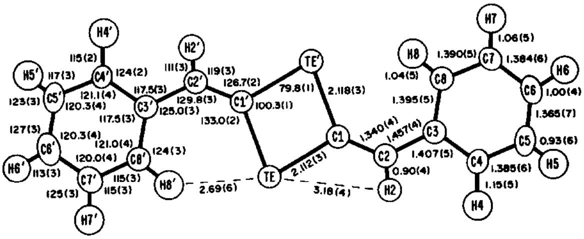


Figure 1. A plot of the molecule showing bond lengths and angles with estimated standard deviations in parentheses.

References and Notes

1. M. L. Petrov, V. Z. Laishev, and A. A. Petrov, *Zh. Org. Khim.* 15, 2596 (1979).
2. Dimethyl sulfoxide was used as a cosolvent.
3. R. Mayer, B. Hunger, R. Prousa, and A. K. Muller, *J. Prakt. Chem.* 35, 294 (1967).
4. Only slightly soluble in hot DMF (recrystallization solvent in Ref. 1) and other high-boiling solvents such as chlorobenzene.
5. For ditellurole 1, Ref. 1 reported the following NMR (δ, ppm), (HMPA): CHPh 7.42, CHTe 9.48, Ph 7.73 m.
6. Ortho H at δ 6.79 ppm, para at 7.10 and meta at 7.40.
7. Crystals suitable for X-ray analysis were obtained from chlorobenzene solution. Crystal data: monoclinic, a = 14.088(2), b = 5.835(2), c = 8.553(2) Å, β = 91.47(2)°, V = 702.9(5) $Å^3$, Z = 2, D_{calc} = 2.171 g/cm^{-3}, D_{obs} = 2.12, space group $P2_1/c$ (from systematic absences). The intensities of 2049 reflections for $2\theta<60°$ were collected on an Enraf-Nonius CAD-4 diffractometer with graphite MoK_α radiation. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was made.[8] The structure was solved by the heavy-atom method and refined, with anisotropic temperature factors for non-hydrogen atoms, by full-matrix least squares.[9] Hydrogen atom positions were calculated and included in the final refinement cycles. All reflections were included in the refinement which converged to R = 0.045.
8. A. C. T North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr.* A24, 351-359 (1968).
9. The programs used for this study were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revision 3-B, 1980.
10. L. Pauling, "The Nature of the Chemical Bond," 3rd. ed., Cornell University Press: Ithaca, New York, 1960, p. 260.

(Received in USA 20 January 1981)