

Organotellurium Chemistry. *cis*- and *trans*-2,6-Diphenyl-1,4-ditellurafulvenes

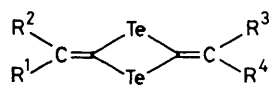
By M. V. LAKSHMIKANTHAM, MICHAEL P. CAVA, MICHAEL ALBECK, and LARS ENGMAN
(Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104)

and FRED WUDL and ELIEZER AHARON-SHALOM
(Bell Laboratories, Murray Hill, New Jersey 07974)

Summary Protonation of sodium phenylethynyltelluroate with trifluoroacetic acid afforded *trans*-2,4-dibenzylidene-1,3-ditelluretan as the minor product, and *cis*- and *trans*-2,6-diphenyl-1,4-ditellurafulvenes (**4**) and (**5**) as the major products which latter represent the first examples of 1,3-ditelluroles.

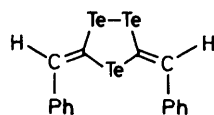
THE protonation of sodium phenylethynyltelluroate by ethereal HCl was reported by Petrov *et al.* to give a crystalline compound, m.p. 270—275 °C, which was assigned the *cis*-ditellurafulvene structure (**4**).¹ Reinvestigation of this reaction under the reported conditions led to the conclusion, based upon X-ray crystallography, that Petrov's compound

was in reality *trans*-2,4-dibenzylidene-1,3-ditelluretan (**1**).^{2,3} The only other products isolated were the *cis* isomer (**2**) of ditelluretan (**1**),³ and *cis*-3,5-dibenzylidene-1,2,4-tritellurole (**3**).²

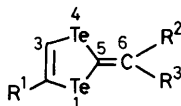


(1) $R^1 = R^3 = \text{Ph}$, $R^2 = R^4 = \text{H}$

(2) $R^1 = R^4 = \text{Ph}$, $R^2 = R^3 = \text{H}$



(3)



(4) $R^1 = R^3 = \text{Ph}$, $R^2 = \text{H}$

(5) $R^1 = R^2 = \text{Ph}$, $R^3 = \text{H}$

(6) $R^1 = R^2 = \text{Ph}$, $R^3 = \text{NO}$

(7) $R^1 = R^3 = \text{Ph}$, $R^2 = -\text{N}=\text{N}-\text{Ph}$

We have now found that protonation of sodium phenylethynyltelluroate with trifluoroacetic acid affords the *trans*-1,3-ditelluretan (**1**) as a minor product (1%), the major products (**5** and **7**%, respectively) being the *cis* and

trans isomers (**4**) and (**5**) of 2,6-diphenyl-1,4-ditellurafulvene. The *cis*-fulvene (**4**) formed fine yellow needles, m.p. 170 °C; δ [(CD₃)₂SO] 8.85 (1H, s, 3-H), 7.86 (1H, s, 6-H), and 7.08—7.50 (10H, m, 2 Ph); $M^+ m/e$ 464 (¹³⁰Te). The *trans*-fulvene (**5**) formed shiny yellow plates, m.p. 235—240 °C; δ [(CD₃)₂SO] 8.77 (1H, s, 3-H), 7.91 (1H, s, 6-H), and 7.08—7.45 (10H, m, 2 Ph); $M^+ m/e$ 464 (¹³⁰Te).

A trace of acid catalyses the interconversion of (**4**) and (**5**) in solution (CDCl₃ or Me₂SO) into a 1:1 mixture of the two isomers. Compounds (**4**) and (**5**) exhibit one irreversible anodic wave $E_p^a = 740 \pm 20$ mV (CH₂Cl₂, 0.1 M Bu₄N⁺ClO₄⁻, 200 mV/s).

The known dithia- and diselena-analogues of (**4**) and (**5**) are readily converted into characteristic stable 6-nitroso-derivatives and red 6-phenylazo-derivatives.⁴ In an analogous manner, the fulvenes (**4**) and (**5**) react with isopentyl nitrite in methylene chloride to give iridescent green crystals of the nitroso-compound (**6**), m.p. 254—256 °C; δ [(CD₃)₂SO] 10.08 (1H, s, 3-H) and 7.42—7.85 (m, 2 Ph); $M^+ m/e$ 493 (¹³⁰Te). Both (**4**) and (**5**) react with benzenediazonium tetrafluoroborate in *NN'*-dimethylformamide to give reddish violet crystals of azo-compound (**7**), m.p. 187 °C (decomp.); δ [(CD₃)₂SO] 9.36 (1H, s, 3-H) and 7.40—8.00 (m, 2 Ph); $M^+ m/e$ 568 (¹³⁰Te).

This work was supported primarily by grants from the N.S.F. Partial support for one of us (L. E.) from Stiftelsen Blanceflor-Boncompagnie-Ludovisi and Signeuls Fond is also gratefully acknowledged.

(Received, 27th April 1981; Com. 500.)

† Satisfactory elemental analyses were obtained for compounds (**4**)—(**7**). The stereochemistry of (**4**) and (**5**) is assigned by analogy with that of their S and Se analogues, in which the less soluble, higher melting isomers have the *trans* configuration (see ref. 4). The stereochemistry of (**6**) and (**7**) is arbitrarily assigned.

¹ M. L. Petrov, V. Z. Laishev, and A. A. Petrov, *Zh. Org. Khim. (Engl. Transl.)*, 1979, **15**, 2346.

² M. V. Lakshmikantham, M. P. Cava, M. Albeck, L. Engman, P. Carroll, J. Bergman, F. Wudl, and E. Aharon-Shalom, *J. Am. Chem. Soc.*, submitted for publication; presented at the 181st National Meeting of the American Chemical Society in Atlanta, April 1st, 1981.

³ S. L. Bender, N. F. Haley, and H. R. Luss, *Tetrahedron Lett.*, 1981, **22**, 1495.

⁴ M. P. Cava and M. V. Lakshmikantham, *J. Heterocycl. Chem.*, 1980, **17**, S-39.