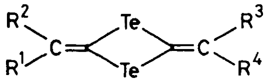
# Organotellurium Chemistry. *cis*- and *trans*-2,6-Diphenyl-1,4-ditellurafulvenes

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)

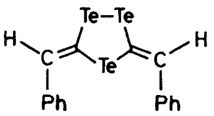
*Summary* Protonation of sodium phenylethynyltellurolate with trifluoroacetic acid afforded *trans*-2,4-dibenzylidine-1,3-ditelluretan as the minor product, and *cis*- and *trans*-2,6-diphenyl-1,4-ditellurafulvenes (**4**) and (**5**) as the major products which latter represent the first examples of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

THE protonation of sodium phenylethynyltellurolate 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-dibenzylidine-1,3-ditelluretan (**1**).[2,3] The only other products isolated were the *cis* isomer (**2**) of ditelluretan (**1**),[3] and *cis*-3,5-dibenzylidine-1,2,4-tritellurole (**3**).[2]

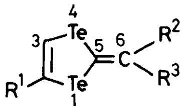


(1) $R^1 = R^3 = Ph,\ R^2 = R^4 = H$

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



(3)



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

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

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

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

We have now found that protonation of sodium phenylethynyltellurolate 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 [$(CD_3)_2SO$] 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 ($^{130}$Te). The *trans*-fulvene (**5**) formed shiny yellow plates, m.p. 235—240 °C; δ [$(CD_3)_2SO$] 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 ($^{130}$Te).

A trace of acid catalyses the interconversion of (**4**) and (**5**) in solution ($CDCl_3$ or $Me_2SO$) 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 ($CH_2Cl_2$, 0·1 M $Bu_4N^+ClO_4^-$, 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 [$(CD_3)_2SO$] 10·08 (1H, s, 3-H) and 7·42—7·85 (m, 2 Ph); $M^+$ *m/e* 493 ($^{130}$Te). 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 [$(CD_3)_2SO$] 9·36 (1H, s, 3-H) and 7·40—8·00 (m, 2 Ph); $M^+$ *m/e* 568 ($^{130}$Te).

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† 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.