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Isolation of Tetraphenylselenurane

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ABSTRACT: *Tetraphenylselenurane has been isolated and structurally characterized by a single crystal structure determination. ($a = 1752.1(7)$, $b = 99.6()$, $c = 1074.2(4)$ pm, $ß = 98.97(1)^\circ$, $P2_1/c$) It is a yellow crystalline material that explodes on warming to room temperature.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:576–578, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20686

INTRODUCTION

The story of phenyl chalcogenurans began with G. Wittig already in 1952[1], when $Te(C_6H_5)_4$ was isolated as a stable compound. Thirty years later its crystal structure was determined [2]. Akiba and Seppelt even managed to obtain $Te(C_6H_5)_6$ and derivatives as compounds stable up to 300°C [3]. Hellwinkel showed that tetraphenylselenurane might be isolated since he managed to obtain the bis(biphenylene) selenurane [4]. Finally, Furukawa et al. could show that reactions of triphenylselenuranium bromide or diphenyl selenoxide with phenyl lithium obviously produced tetraphenylselenurane in solution at −100°C. Clear evidences were ^{77}Se, ^{13}C, and ^{1}H NMR spectra [5]. It was also shown that the decomposition in THF resulted in diphenylselenium and diphenyl with an activation energy of 21.3 kcal mol^{-1} [6]. The aim of the present study is to completely establish the identity of $Se(C_6H_5)_4$.

RESULTS

The method chosen for preparing $Se(C_6H_5)_4$ was slightly different than described in [5,6]. Rather than reacting $(C_6H_5)_3Se^+Br^-$ or $(C_6H_5)_2SeO$ with C_6H_5Li, we have used $(C_6H_5)_2SeF_2$ as a starting material. $(C_6H_5)_2SeF_2$ has been prepared by fluorination of $(C_6H_5)_2Se$ with XeF_2 in essentially qualitative yield. According to its spectral data, it is identical to the material described before, where it has been prepared by fluorination of $(C_6H_5)_2SeCl_2$ [7]or $(C_6H_5)_2Se$ [8] with XeF_2.

The reaction of $(C_6H_5)_2SeF_2$ with C_6H_5Li in $(C_2H_5)_2O$ between −78 and −40°C afforded $(C_6H_5)_4Se$ in essentially quantitative yield. The ^{77}Se NMR resonance at $\delta = 377.7$ pm is very close to a previous report (373.7 ppm). In the solid state it is yellow and decomposes violently upon warming to room temperature. In the crystal, the compound appears in isolated molecules with little intermolecular interactions. The environment of the selenium atom is pseudo-trigonal bipyramidal, as expected. Two longer (214.9(4), 219.9(4) pm) axial Se—C bonds form an almost linear array (179.2(2)°), and two shorter equatorial bonds (193.2(4), 194.4(4) pm have an angle of 105.48(2)°; see Table 1 and Fig. 1.

DISCUSSION

While $Se(C_6H_5)_4$ has now been isolated, its decomposition into $Se(C_6H_5)_2$ and $(C_6H_5)_2$ [6] hampers further investigations. Attempts to fluorinate it further by XeF_2 with the aim to get $(C_6H_5)_4SeF_2$, similar to the procedure of *cis*-$C_6H_5)_4TeF_2$ [3] or *cis*−(biphenyl)$_2SeF_2$ [9] failed completely. The compound $Se(C_6H_5)_6$ is therefore presently out of reach.

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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TABLE 1 Bond Lengths (pm) and Angles (°) in $Se(C_6H_5)_4$

$Se{-}C_{ax}$	193.2(4), 194.4(4)
$Se{-}C_{eq}$	214.9(4), 219.9(4)
$C_{ax}{-}Se{-}C_{ax}$	179.2(2)
$C_{eq}{-}Se{-}C_{eq}$	105.5(2)

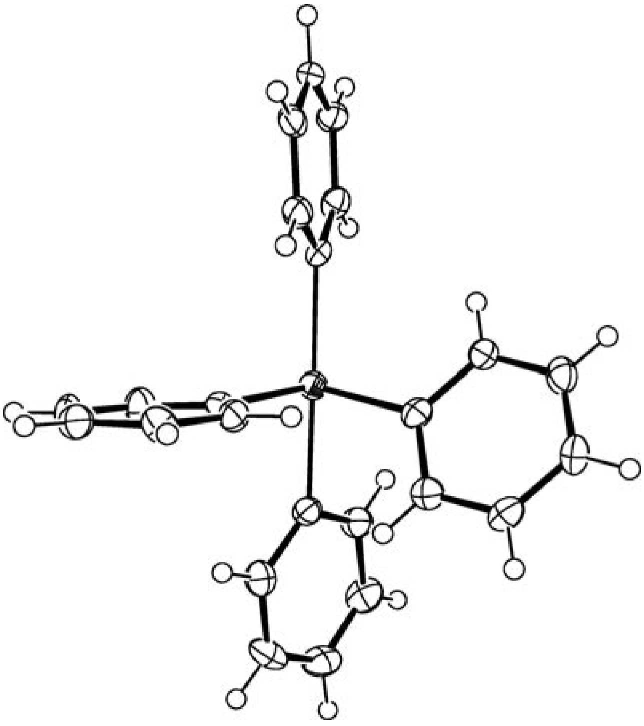

FIGURE 1 Structure of $Se(C_6H_5)_4$ in the crystal, Ortep representation, 50% probability ellipsoids.

The existence of the sulfur analogue $S(C_6H_5)_4$ as an intermediate has already been raised by Furukawa et al. [9], but isolation would have to be done at −100°C or below. Bis(biphenyl)sulfurane, however, is stable at room temperature [10].

We have not been able to isolate the perfluorinated analogue, $Se(C_6F_5)_4$, although it should exhibit greater stability. Main difficulty has been to obtain $(C_6H_5)_2SeF_2$ in relatively pure form.

EXPERIMENTAL

Material

$(C_6H_5)_2Se$ and $C_6H_5{-}Li$ solution in $(C_4H_9)_2O$ were purchased from Aldrich Co. and distilled at 75°/10^{-3} mbar. XeF_2 was prepared from the elements under UV irradiation [11].

Instrumentation

NMR spectra were recorded on a JEOL multinuclear instrument at 400 MHz for ^{1}H. Chemical shifts given are relative to TMS, $CFCl_3$, and $(CH_3)_2Se$. Raman spectra were recorded on a RFS 100/S Bruker instrument with neodym YAG laser excitation.

Crystal Structure Determination

Bruker Smart CCD 1000 TU diffractometer, Mo Kα radiation, graphite monochromator, scan width of 0.3° in ω, a total of 1800 frames with 10 s per frame. Semiempirical absorption correction (SADABS), as implemented in the diffractometer software, by equalizing symmetry equivalent reflections. All atoms except hydrogen are refined anisotropically; hydrogen atoms are refined isotropically. Experimental details are summarized in Table 2; further experimental details can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif. by quoting the CCDC number 780535.

$(C_6H_5)_2SeF_2$. 0.42 g (1.8 mmol) diphenylselenium was added dropwise to a solution of (2.0 mmol) XeF_2 in CH_2Cl_2 at −20°C in an argon atmosphere. During 2 h stirring, the mixture was allowed to 0°C while the color changed from orange over brown to deep purple. After further stirring for 1 h at room temperature, the solvent was removed in vacuum, yielding a dark purple crystalline solid.

^{19}F NMR (CH_2Cl_2): $\delta = -67.18$ ppm, $^{1}J\,^{19}F\text{-}^{77}Se = 533.9$ Hz; $^{77}Se\{^{19}F\}$ NMR (CH_2Cl_2): 783 ppm; 7.47–7.43 (ortho, para) ^{1}H NMR (CH_2Cl_2): 7.89–7.87 (meta).

TABLE 2 Experimental Details of the Crystal Structure of $Se(C_6H_5)_4$

μ	387.36
a (pm)	1752.1(7)
b (pm)	994.6(4)
c (pm)	1074.2(4)
β (deg)	98.97(1)
V (10^6 pm^3)	1848.9
Space group	$P2_1/c$, monoclinic
Color	Yellow
Size (mm)	0.1 × 0.05 × 0.05
T (°C)	−140
θ_{max} (deg)	52.0
Reflections	
Measured	10974
Unique	3610
Parameters	226
$R_1(F_o > 4\sigma(F_o))$	0.0464
R_1 (all data)	0.0906
wR_2	0.1040
Goodness of fit	0.985

$(C_6H_5)_4Se$. 2 mL (3.6 mmol) C_6H_5Li (1.8 mol/L in $(C_4H_9)_2O$) was added dropwise to a solution/suspension of $(C_6H_5)_2SeF_2$ (0.49 g, 1.8 mmol) in 10 mL $(C_2H_5)_2O$ at −78°C under dry argon. During 2 h stirring, the mixture was warmed to −45°C. The color of the solution changed from green to yellow-orange, and LiF precipitated. After rapid filtration, a part of the solvent was removed in vacuum and the product was crystallized at −78°C, yielding small yellow brick-shaped crystals. At ambient temperature, $(C_6H_5)_4Se$ crystals decompose violently.

^{77}Se NMR (Et_2O, Bu_2O): 377.8 ppm. Raman (−100°): 3058(14), 3039(5), 3021(5), 1562(16), 1064(16), 1022(28), 1002(72), 898(17), 732(20), 666(25), 629(73), 612(27), 490(28), 480(31), 345(27), 279(27), 234(45), 217(39), 162(100) cm^{-1}.

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