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REACTION OF BENZYLTRIMETHYLSILANE WITH TELLURIUM(IV) CHLORIDE. STRUCTURE OF BIS(*p*-TRIMETHYLSILYLTOLYL)-TELLURIUM DICHLORIDE

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Summary

The reaction of $TeCl_4$ with benzyltrimethylsilane in toluene gives condensation products, p-$Me_3SiCH_2C_6H_4TeCl_3$ and $(p$-$Me_3SiCH_2C_6H_4)_2TeCl_2$. Crystals of the latter are orthorhombic with space group *Pbcn* *a* 17.890(5), *b* 17.047(7) and *c* 8.169(3) Å and $Z = 4$. The structure refined to a final R value of 0.0327 for 1490 unique "observed" reflections. The compound adopts a four-coordinate geometry with two Te $\cdots$ Cl secondary interactions completing a distorted octahedral configuration about the tellurium atom.

Introduction

It has been known for some time that $TeCl_4$ reacts with aromatic hydrocarbons bearing activating substituents such as RO, RCO, HO, R_2N, RS etc., in an organic solvent to give mixtures of $RTeCl_3$ and R_2TeCl_2 [1]. Less reactive species such as benzene or toluene do not react under these conditions although the reaction proceeds in the presence of a Lewis acid, such as $AlCl_3$ [2,3]. However, CH_2SiMe_3 has been shown to be a stronger activating substituent group than CH_3 due to hyperconjugation [4,5] and is therefore, expected to give condensation products with $TeCl_4$. This reaction, to our knowledge, has never been studied. In this paper we, therefore, describe the reaction of $C_6H_5CH_2SiMe_3$ with $TeCl_4$ and the crystal structure of one of the products, $(p$-$Me_3SiCH_2C_6H_4)_2TeCl_2$, (**B**).

Results and discussion

Two new products, p-$Me_3SiCH_2C_6H_4TeCl_3$, (**A**), and $(p$-$Me_3SiCH_2C_6H_4)_2TeCl_2$, (**B**), have been prepared by the condensation reaction between $C_6H_5CH_2SiMe_3$ and

$TeCl_4$:

$$C_6H_5CH_2SiMe_3 + TeCl_4 \xrightarrow[\text{toluene,}\ -HCl]{12\ h} p\text{-}Me_3SiCH_2C_6H_4TeCl_3 + (p\text{-}Me_3SiCH_2C_6H_4)_2TeCl_2$$

Equimolar quantities of the reactants were refluxed in toluene for 12 h and the products were obtained in rather poor yields of 20 and 10% for **A** and **B** respectively by reducing the volume of the solution. The reaction with two molar equivalents of $C_6H_5CH_2SiMe_3$ and increased reflux time (48 h) gave a better yield of **B**, 45%, but a poorer yield of **A**, 10%. The yield of **A** was improved by the addition of one molar equivalent of anhydrous $AlCl_3$ to the reaction mixture. The reaction gave the optimum yield of **A** (50%) when it was carried out at 80°C and when the reflux time was reduced to 10 h. However, all attempts to isolate a single product instead of the mixture of **A** and **B** were unsuccessful.

Both the products are white in color and are insensitive to aerial decomposition. **A** is only sparingly soluble in toluene, while **B** is soluble in CH_2Cl_2, $CHCl_3$ and benzene.

The four line *AA'BB'* signals of the phenyl protons in the ^1H NMR spectra of both the products suggest that only *para*-substituted products are obtained, which is confirmed by the crystal structure determination of **B**. It is interesting to note that a Me_3Si group on an aromatic ring, on the contrary, directs the substitution at the *ipso* position, e.g. p-$RC_6H_4SiMe_3$ reacts with $TeCl_4$ to give p-$RC_6H_4TeCl_3$ and Me_3SiCl [6], probably due to the ease of cleavage of the Si–Ar bond.

Interpretation of the IR spectra (600–50 cm^{-1}) of the products has been done according to McWhinnie et al. [7,8]. Strong bands in the region 330–293 cm^{-1} in the IR spectrum of **A** are associated with Te–Cl stretching vibrations, while the bands at 243 and 220 cm^{-1} may be assigned to Te–C stretching modes. The IR spectrum of **B** shows many bands, out of which bands at 280 and 252 cm^{-1} may have contributions from Te–Cl stretching vibrations and bands at 252 and 237 cm^{-1} may have contributions from Te–C stretching vibrations. The other bands up to 200 cm^{-1} in both the products are probably due to the phenyl modes and the bands below 200 cm^{-1} arise from the deformation modes.

The crystals of **B** consist of discrete molecules shown in Fig. 1. The compound adopts a primary four-coordinate geometry which may be considered as based on a distorted trigonal bipyramid with an equatorial lone pair. The axial chlorine atoms and equatorial p-$Me_3SiCH_2C_6H_4$ groups are related by a two-fold axis bisecting the CTeC bond. Te–C and Te–Cl bond lengths and CTeC bond angles (Table 3) are within the range found for other R_2TeCl_2 compounds [9–14]. The tellurium atom is involved in intermolecular interactions with two chlorine atoms of the neighbouring molecules (at a distance of 3.615(1) Å). These secondary interactions, complete a distorted octahedral configuration about tellurium atoms, as has been found in previous structures of R_2TeCl_2, with the exception of Ph_2TeCl_2 [11], and link the molecules into infinite chains parallel to the crystallographic *c* axis, which results in the crystal growth along this axis. A view of the structure normal to one of the chains is shown in Fig. 2. The intermolecular bonding arrangment in the present structure is thus similar to that in phenoxatellurin 10,10-diiodide [15] dibenzotellurophene diiodide [16], and α-1,1-diiodo-3,4-benzo-1-telluracyclopentane [17] in

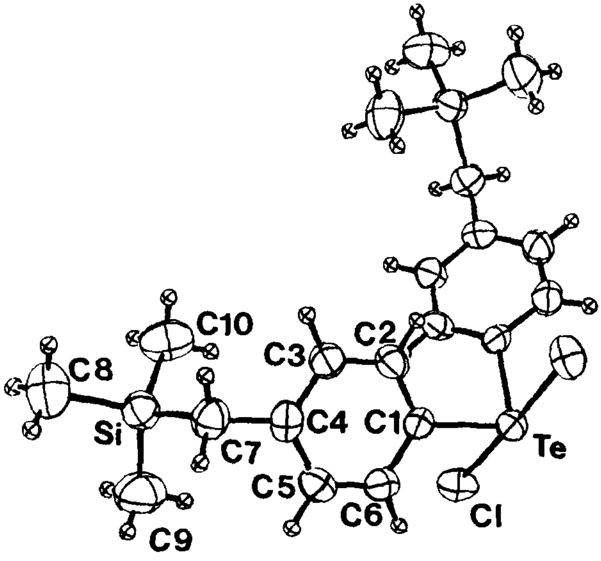

Fig. 1. Molecular structure of $[p\text{-}(CH_3)_3SiCH_2C_6H_4]_2TeCl_2$. The ellipsoids correspond to 50% probability. The labeling scheme is defined, unlabeled atoms are related to labeled ones by a two-fold. Hydrogen atoms are drawn arbitrarily small.

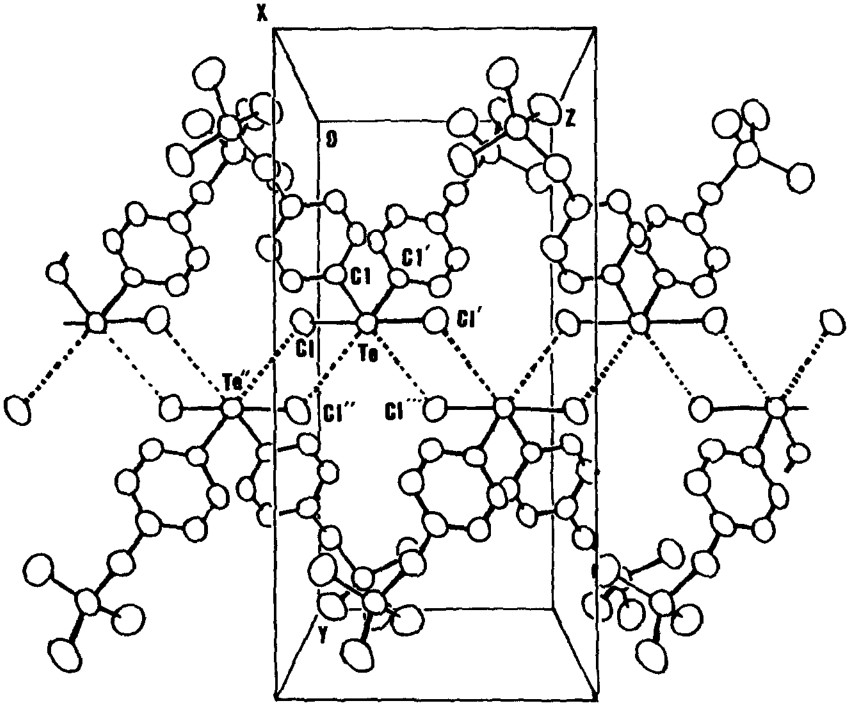

Fig. 2. View normal to the chains formed by the Te · · · Cl secondary bonds, which are shown by means of dotted lines. The hydrogen atoms are omitted for clarity.

which the chains are parallel to *a*, *b* and *c* axes respectively.

The angles between the TeCC plane and the phenyl rings are 38.7 * and 141.3°. The phenyl rings are rotated by 127.9 and 52.1° with respect to C(1)TeCl and C(1)'TeCl' respectively so that as was found earlier in (*p*-BrPh)$_2$TeCl$_2$ [10] and (*p*-BrPh)PhTeCl$_2$ [9], the rings are in a propeller rather than a butterfly arrangement.

The *para*-substituent Me$_3$SiCH$_2$ on the phenyl ring adopts a regular tetrahedral configuration about silicon with average C–Si–C angle of 109.4(3)°. The average Si–C distance of 1.860(5) Å is in good agreement with the reported values of 1.856(11) [18] and 1.867(3) Å [19].

Experimental

$C_6H_5CH_2SiMe_3$ and $TeCl_4$ were purchased from Petrarch and Alfa Products respectively and used as such. Solvents were purified by the standard methods. IR spectra were recorded in Nujol mulls on a Perkin–Elmer 180 spectrophotometer in CsI and polyethylene disks. ^{1}H NMR spectra were recorded at 60 MHz using a Varian EM-360 instrument. Carbon, hydrogen and chlorine microanalyses were performed by Guelph Chemical Laboratories Ltd., and tellurium was determined using standard gravimetric techniques. The density was measured by the flotation method in CCl_4/CH_3I. All reactions were carried out in anhydrous conditions.

Synthesis of compounds

$C_6H_5CH_2SiMe_3$ (5.44 g, 0.033 mol) was added to a solution of $TeCl_4$ (8.96 g, 0.033 mol) in 100 ml of toluene. The reaction mixture was refluxed for 12 h, cooled to room temperature and filtered to remove the insoluble impurities. The filtrate was concentrated under vacuum to 20 ml and left overnight. A white precipitate, which separated, was recrystallised from a large volume of toluene to give *p*-$Me_3SiCH_2C_6H_4TeCl_3$, (**A**), (2.69 g; yield 20%), m.p. 172–175°C. Anal. Found: C, 29.64; H, 3.84; Cl, 26.02; Te, 31.75. $C_{10}H_{15}Cl_3SiTe$ calcd.: C, 30.21; H, 3.78; Cl, 26.81; Te, 32.13%. IR (cm^{-1}): 477s, 330s, 316m, 293s, 243m, 220w, 181s, 133vs, 78w. ^{1}H NMR ($CDCl_3$: DMSO-d_6): δ 0.01 (s, 9H, Me$_3$Si), 2.46 (s, 2H, SiCH$_2$), 7.41 (dd, 2H *meta*-Ar–H), 8.42 (dd, 2H, *ortho*-Ar–H). Suitable crystals of **A** for single crystal X-ray analysis, however, could not be obtained because the product was microcrystalline.

The mother liquour after the separation of **A** was diluted with 100 ml of CH_3CN and left covered for 3 d. The white precipitate which separated slowly, was filtered, washed with CH_3CN and dried in vacuo. Recrystallisation of the crude product from CH_2Cl_2 gave needles of (*p*-$Me_3SiCH_2C_6H_4)_2TeCl_2$, (**B**), (1.7 g, 10%) suitable for X-ray analysis, m.p. 184–186°C. Anal. Found: C, 45.96; H, 6.09; Cl, 12.81; Te, 24.00. $C_{20}H_{30}Cl_2Si_2Te$ calcd.: C, 45.70; H, 5.71; Cl, 13.52; Te, 24.29%. IR (cm^{-1}): 622m, 600s, 580s, 490s, 364m, 360m, 329m, 280m, 252s, 237s, 228s, 178w, 128m, 120m, 70w. ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 9H, Me$_3$Si), 2.22 (s, 2H, SiCH$_2$), 7.30 (dd, 2H, *meta*-Ar–H), 8.10 (dd, 2H, *ortho*-Ar–H).

A similar reaction was set up for two molar equivalent of $C_6H_5CH_2SiMe_3$. The reaction was refluxed for 48 h and worked up as described in the previous

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* e.s.d.'s for the dihedral angles are ~ 1.0°.

experiment. The yields of **A** and **B** were 10 and 45% respectively.

In another reaction, equimolar quantities of the reactants were refluxed for 1 h. The temperature was lowered to 50°C and one molar equivalent of anhydrous $AlCl_3$ was added. Evolution of HCl ensued. The reaction was stirred for another 10 h at 80°C, allowed to cool, filtered to remove inorganic impurities. Upon concentration of the reaction volume to 1/4, the white product was characterised to be **A** in 50% yield. The mother liquour gave 5–10% of **B**.

Crystal structure determination

A single crystal of **B** with approximate dimensions 0.15 × 0.19 × 0.39 mm was mounted along the largest dimension, subsequently shown to be the *c* axis, and data were collected on a Syntex $P2_1$ diffractometer following the procedure described previously [9]. The intensities of three monitor reflections did not change significantly during data collection. A non-standard space group *Pnab* was determined from systematic absences, $0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$; $hk0$, $k = 2n + 1$. The matrix (0 0 1 0 1 0 −1 0 0) was used to transform the data to standard setting of *Pbcn* (No. 60). The data were corrected for absorption, Lorentz and polarisation effects. Details of X-ray data are given in Table 1.

The position of the tellurium atom was obtained from a sharpened Patterson synthesis with the tellurium atom on the two-fold axis. The positions of remaining non-hydrogen atoms were determined from a difference Fourier map. The structure

TABLE 1

CRYSTALLOGRAPHIC DATA

a (Å)	17.890(5)
b (Å)	17.047(7)
c (Å)	8.169(3)
V (Å^3)	2491.2(15)
Crystal system	orthorhombic
Space group	*Pbcn*
Mol. wt.	524.8
Z	4
ρ_c (g cm^{-3})	1.37
ρ_o (g cm^{-3})	1.40
Radiation	Mo-K_α, λ 0.71069 Å
Monochromator	highly oriented graphite
Temp. (°C)	21
Abs. coeff., μ (cm^{-1})	13.9
Min abs. corr.	1.216
Max abs. corr.	1.265
2θ angle (°)	4–50
Scan type	coupled θ (crystal)/2θ (counter)
Scan width	$K_{\alpha_1} - 1°$ to $K_{\alpha_2} + 1°$
Scan speed (° min^{-1})	variable, 2.02–4.88
Bkgd time/scan time	0.5
Total reflcns measd	2690 ($+h$, $+k$, $+l$)
Unique data used	1490 [$I > 3\sigma(I)$]
No. of parameters (NP)	114
R	0.0327
R_wF	0.0362

TABLE 2

FINAL FRACTIONAL COORDINATES AND ISOTROPICAL THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS OF $[p\text{-}(CH_3)_3SiCH_2C_6H_4]_2TeCl_2$ WITH STANDARD DEVIATIONS IN PARENTHESES.

	x	y	z	U_{eq} [a] ($Å^2 \times 10^3$)
Te	0.50000	0.42477(2)	0.25000	43.9(2)
Cl	0.4192(1)	0.4214(1)	−0.0019(2)	62(1)
Si	0.6701(1)	0.1019(1)	−0.2159(2)	56(1)
C(1)	0.5710(3)	0.3425(2)	0.1392(5)	42(2)
C(2)	0.5918(3)	0.2751(3)	0.2210(5)	47(3)
C(3)	0.6393(3)	0.2222(3)	0 1498(5)	49(3)
C(4)	0.6698(3)	0.2346(3)	−0.0039(6)	48(3)
C(5)	0.6493(3)	0 3026(3)	−0.0857(6)	60(3)
C(6)	0.5997(3)	0.3553(3)	−0.0169(6)	58(3)
C(7)	0.7194(3)	0.1742(3)	−0.0818(6)	54(3)
C(8)	0.7383(4)	0.0235(4)	−0.2681(6)	87(4)
C(9)	0.6368(4)	0.1533(4)	−0.4012(7)	92(4)
C(10)	0.5884(3)	0.0601(3)	−0.1045(8)	82(4)

[a] U_{eq} for the non-hydrogen atoms is calculated from the refined anisotropic thermal parameters ($U_{eq} = 1/3 \sum_{i=1}^{3} (\mathrm{RMSD})_i^2$, RMSD values are taken from ORTEP output.).

TABLE 3. INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Te–Cl	2.516(1)	Cl–Te–C(1)	88.9(1)
		Cl′–Te–C(1)	89.4(1)
Te–C(1)	2.098(4)	Cl–Te–Cl′	177.4(2)
		C(1)–Te–C(1)	96.1(2)
C(1)–C(2)	1.380(5)	Te–C(1)–C(2)	120.7(3)
C(1)–C(6)	1.391(5)	Te–C(1)–C(6)	120.9(3)
C(2)–C(3)	1.369(5)	C(2)–C(1)–C(6)	118.4(4)
C(3)–C(4)	1.385(5)	C(1)–C(2)–C(3)	120.6(4)
C(4)–C(5)	1.387(6)	C(2)–C(3)–C(4)	121.9(4)
C(4)–C(7)	1.501(6)	C(3)–C(4)–C(5)	117.4(4)
C(5)–C(6)	1.383(6)	C(3)–C(4)–C(7)	120.8(4)
Si–C(7)	1.870(4)	C(5)–C(4)–C(7)	121.7(4)
Si–C(8)	1.859(5)	C(4)–C(5)–C(6)	121.2(4)
Si–C(9)	1.848(5)	C(1)–C(6)–C(5)	120.4(4)
Si–C(10)	1.863(5)	C(4)–C(7)–Si	114.9(3)
		C(7)–Si–C(8)	107.3(2)
		C(7)–Si–C(9)	108.6(2)
Te ··· Cl″	3.615(1)	C(8)–Si–C(9)	111.4(3)
Te ··· Te″	4.823(1)	C(7)–Si–C(10)	109.7(2)
		C(8)–Si–C(10)	110.6(3)
		C(9)–Si–C(10)	109.2(3)
		Cl′–Te ··· Cl‴	77.8(2)
		Cl′–Te ··· Cl″	104.2(2)
		Cl‴ ··· Te ··· Cl″	87.0(2)
		C(1)–Te ··· Cl″	90.1(3)
		C(1)–Te ··· Cl‴	165.7(3)
		Te–Cl ··· Te″	102.2(2)

Symmetry equivalent positions, $' = 1 - x, y, 0.5 - z$

$'' = 1 - x, 1 - y, -z$

$''' = x, 1 - y, 0.5 + z$

was refined anisotropically by the full matrix least squares methods. The refinement converged to $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.414$. A difference map at this stage showed peaks at plausible hydrogen positions. Hydrogen atoms were included in subsequent refinements in ideal positions (C–H 0.95 Å and CCH 120 or 109.5°). Refinements gave final values of $R = 0.0327$ and $R_{wF} = [\Sigma_w\Delta^2/\Sigma_w F_o^2]^{1/2} = 0.0362$. In the final two cycles of refinement the largest shift/error ratio was 0.04 and the final difference map had no feature of chemical significance with the largest peak 0.5 eÅ^{-3}. The function $(|F_o| - |F_c|)^2$ was minimised during least squares refinement and in the final cycles, a weighting scheme of the form $\omega = 1/[\sigma^2(F) + \rho F^2]$ was employed with a final ρ value of 0.000064. No evidence of secondary extinction was found.

Sources of scattering factors and computer programs used have been given elsewhere [9]. The final atomic coordinates for non-hydrogen atoms are given in Table 2 and important distances and angles in Table 3. List of structure factors, anisotropic thermal parameters and fractional coordinates for hydrogen atoms may be obtained from the authors.

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