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Preparation of 2-phenyl-2-iodo-5,6-dimethyl-1,3-dihydro-2-telluraindene. Phenylation at tellurium by tetraphenylborate ion

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Abstract

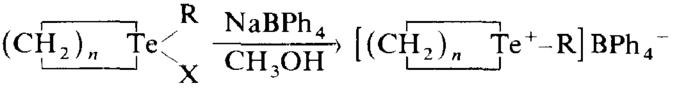
Reaction of 1,2-bis(chloromethyl)-4,5-dimethylbenzene with tellurium powder and sodium iodide gives the red-orange 2,2-diiodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (I). Compound I reacts with sodium tetraphenylborate under mild conditions to give a compound for which elemental analysis, molar conductivity, IR, ^{1}H NMR and ^{13}C NMR and mass specroscopy suggest that it is 2-phenyl-2-iodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (II), formed as unexpected product. Some other new compounds are reported.

Introduction

Ziolo et al. [1] reported that dimethyltellurium dichloride and diphenyltellurium dichloride undergo phenylation by sodium tetraphenylborate in methanolic solution to produce dimethylphenyltelluronium tetraphenylborate and triphenyltelluronium tetraphenylborate, respectively. Structural investigations [2,3] of triorganotelluronium tetraphenylborate compounds have shown them to be example of three coordinate tellurium and indicated no cation–anion interaction.

Our recent works [4–7] demonstrated that the reactions of heterocyclic tellurium dihalides and heterocyclic telluronium halides with $NaBPh_4$ give the corresponding heterocyclic telluronium tetraphenylborate, as shown in eq. 1 and 2.

$$(CH_2)_n\,TeX_2 \xrightarrow[CH_3OH]{NaBPh_4} [(CH_2)_n\,Te^{+}\text{–}Ph]BPh_4^{-} \qquad (1)$$



$$(CH_2)_n\,Te\begin{matrix}R\\X\end{matrix} \xrightarrow[CH_3OH]{NaBPh_4} [(CH_2)_n\,Te^{+}\text{–}R]BPh_4^{-} \qquad (2)$$

Furthermore, the compounds $C_8H_8TeR^+\ BPh_4^-$ [4], $C_4H_8TeR^+\ BPh_4^-$ [5], $C_4H_8OTeR^+\ BPh_4^-$ [6] and $C_5H_{10}TeR^+\ BPh_4^-$ [7] showed low conductivities in dimethylsulphoxide (DMSO) and *N*,*N*-dimethylformamide (DMF).

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In the present work, we attempted the synthesis of the new heterocyclic telluronium tetraphenylborate $[C_{10}H_{12}TePh^+]BPh_4^-$, by treating $C_{10}H_{12}TeI_2$ (I) with $NaBPh_4$. We found that the reaction gave the corresponding 2-phenyl-2-iodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (II) as an unexpected product. We describe below the synthesis and characterization of compounds I, II, and some related compounds.

Experimental

(a) Synthesis

2,2-Diiodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (I). A mixture of 1,2-bis(chloromethyl)-4,5-dimethylbenzene [8] (10.25 g, 50 mmol), sodium iodide (30 g; 200 mmol), and powdered tellurium (6.38 g; 50 mmol) in 2-butoxyethanol (120 cm^3) was stirred under gentle reflux for 4 h. The mixture was then cooled and deionized water (300 cm^3) was added to produce additional precipitate. The precipitate was filtered off, washed with water, air dried, and recrystallized from 2-butoxyethanol to give compound I, as red-orange crystals, m.p. 204–205 °C. Mass spectrum: *m/e* (relative intensity; only peaks stronger than 5% of the base peak above *m/e* 50) 389 (7), 334 (10), 262 (19), 257 (6), 245 (50), 132 (100), 127 (5), 117 (45), 91 (9.5), 77 (13), 51 (21).

2-Phenyl-2-iodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (II). A stirred mixture of $C_{10}H_{12}TeI_2$ (compound I) (2.57 g; 5 mmol) and sodium tetraphenylborate (3.42 g; 10 mmol) in dry ethanol (100 cm^3) was heated for 15 min. The hot solution was filtered, and allowed to cool, and white crystals of compound II were then filtered off in quantitative yield. The product was washed successively with water and ethanol and recrystallized from water/DMF, to give material of m.p. 186 °C. Mass spectrum: *m/e* (relative intensity; only peaks stronger than 5%, except the $C_{10}H_{12}Te(Ph)I^+$ and $C_{10}H_{12}TeI^+$ peaks, of the base peak above *m/e* 50) 466 (4), 389 (5), 339 (12.5), 334 (11), 262 (14), 257 (5), 207 (16), 204 (11.5), 154 (7), 132 (100), 117 (34), 91 (16), 77 (40), 51 (19).

2-Phenyl-5,6-dimethyl-1,3-dihydro-2-telluraindene tetraphenylborate (III). A stirred mixture of $C_{10}H_{12}TeI_2$ (2.57 g; 5 mmol) and sodium tetraphenylborate (3.42 g; 10 mmol) in dry ethanol (100 cm^3) was heated under reflux for 3–4 h. The solution was filtered hot and allowed to cool, and the white precipitate was filtered off and recrystallization from water/DMF to give white crystals of III, m.p. > 300 °C. Mass spectrum: *m/e* (relative intensity; only peaks stronger than 5% of the base peaks above *m/e* 50) 416 (12), 339 (9), 319 (6), 284 (15), 262 (11.5), 242 (28), 207 (17), 165 (70), 163 (60), 154 (160), 139 (10), 137 (19), 132 (33), 117 (24), 113 (12), 91 (56), 88 (11), 77 (45), 51 (18).

2,5,6-Trimethyl-1,3-dihydro-2-telluraindene tetraphenylborate (IV). This compound was first prepared by AL-Masoudi [9]. A mixture of 2,5,6-trimethyl-2-iodo-1,3-dihydro-2-telluraindene (4.02 g; 10 mmol) and sodium tetraphenylborate (3.42 g; 10 mmol) in dry methanol was stirred for 3 h at room temperature, then heated under reflux for 2 h. The white crystals were collected, washed with water then with ethanol, and recrystallized from water/DMF to give white crystals, m.p. 165 °C. Mass spectrum: *m/e* (relative intensity; only peaks stronger than 8% of the base peak above *m/e* 50) 416 (12), 319 (8), 284 (14), 262 (12), 242 (39), 207 (12), 165 (98), 163 (63), 154 (19), 139 (10), 137 (20), 132 (32), 117 (14), 113 (18), 91 (53), 88 (11), 77 (15), 51 (16).

2-Ethyl-5,6-dimethyl-1,3-dihydro-2-telluraindene tetraphenylborate (V). This was prepared by the method described immediately above as white crystals, m.p. 168° C. Mass spectrum: *m/e* (relative intensity, only peaks stronger than 7% of the base peak above *m/e* 50) 416 (13), 319 (10), 284 (20), 262 (10), 242 (25), 207 (15), 165 (72), 163 (42), 154 (10), 139 (7), 137 (14), 132 (42), 117 (27), 113 (11), 91 (79), 88 (12), 77 (32), 51 (19).

(b) Physical measurements

^{1}H NMR spectra were recorded on Bruker WM-250 spectrometer at 250 MHz with TMS as internal reference. ^{13}C NMR spectra were recorded on Bruker AC-250 spectrometer at 61.9 MHz with TMS as internal reference. Infrared spectra (KBr discs) were recorded in the range 4000–200 cm^{-1} on a Pye-Unicam SP3-300s spectrophotometer. Conductivity data were measured with a WTW conductivity meter LBR, using a standard conductivity cell with cell constant of 1.0850.

Mass spectra were measured at 70 eV with MAT 1125 Finnigan mass spectrometer; peaks shown relate to ^{130}Te, ^{11}B and ^{12}C (data for compounds I and IV were obtained from ref. 9).

Microanalyses for carbon and hydrogen by Micro Analytical Service of Fakultät für Chemie, Universität Konstanz, West Germany. Melting points were determined with a Gallenkamp apparatus and are uncorrected.

Results

The compounds considered in this paper are listed in Table 1 with their analytical, IR, and molar conductance data. Table 2 lists ^{1}H NMR data and Table 3 ^{13}C NMR data.

Discussion

The reaction of compound I with sodium tetraphenylborate shows that $NaBPh_4$ readily phenylates one Te–I bond under mild conditions to leave the second Te–I bond intact. When the reaction is carried out under more forcing conditions the corresponding tetraphenylborate derivative, III, is obtained. Other new derivatives containing the BPh_4^- ion were prepared for comparison (see Table 1).

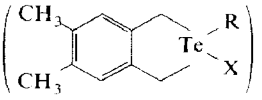
The molar conductance (Table 1) for all the compounds except for the iodo derivatives I and II were lower than expected for 1/1 electrolytes [4–7,10]. This may be due to the close contact between a tellurium atom and one phenyl ring of the BPh_4^- ion, as revealed by X-ray studies on analogous compounds [2,3].

The infrared spectra of all compounds show a band in the regions 430–450 cm^{-1}, and are similar to those assigned to ν(Te–C$_{\text{alkyl}}$) in other heterocyclic [4–7] or dialkyl derivatives [11] of tellurium (Table 1). The ν(Te–C$_{\text{phenyl}}$) bonds for compounds II and III are not significantly different from those reported for the diphenyltelluride unit [12] or for analogous compounds [4–7]. This can be associated with the fact that the two compounds both contain the tellurium cation.

In the ^{1}H NMR spectra the expected ratios of aromatic to aliphatic protons were observed. The cation phenyl-proton multiplets are downfield from the anion phenyl-proton multiplets (see Table 2), which is consistent with the large deshielding effect expected in the cation. The methylene protons (1 and 3, Table 2) appear as a

Table 1

Analytical, IR and conductivity data for the new compounds.



Compound		M.p. (°C)	Analysis [a] (%)		IR data (ν(cm^{-1}))	Solvent/molar conductance (ohm^{-1} cm^2 mol^{-1})	
R	X		C	H		DMSO [b]	DMF [b]
I	I	204–205	23.07 (23.38)	1.97 (2.35)	432(ν(Te–C(1,3)))	36.6	54.7
Ph	I	186	40.90 (41.34)	3.65 (3.69)	434(ν(Te–C(1,3))) 258(ν(Te–Ph))	24.8	46.8
Ph	BPh_4	> 300	73.58 (73.22)	5.19 (5.68)	435(ν(Te–C(1,3))) 258(ν(Te–Ph))	13.8	28.3
CH_3	BPh_4	165	70.33 (70.76)	5.99 (5.99	450(ν(Te–C(1,3))) 535(ν(Te–C_{alkyl}))	15.6	33.7
CH_2CH_3	BPh_4	168	70.78 (70.10)	6.17 (6.13)	430(ν(Te–C(1,3)))	17.3	34.5

[a] Calculated values are in parentheses. [b] $[(C_2H_5)_4N]Cl$: Λ_M 30(DMSO); 80(DMF) ohm^{-1} cm^2 mol^{-1}.

singlet for compound I. In the case of the telluronium salts, the presence of an organic group on tellurium atom clearly destroys the equivalence of the two protons within each methylene group, and changes the methylene spectrum to a simple AB pattern as it would be expected for a pyramidal configuration of tellurium–carbon bond. The coupling constant $^2J_{1a1b}(=\,^2J_{2a2b})$ is ca. 15 Hz, a value consistent with sp^3 hybridised carbon [4,13].

The most interesting data for these new compounds are the ^{13}C NMR spectra (Table 3). The aromatic and aliphatic regions were assigned by analogie with earlier

Table 2

^1H NMR data for 5,6-dimethyl-1,3-dihydro-2-telluraindene derivatives

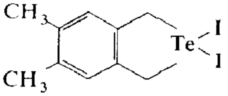
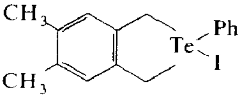
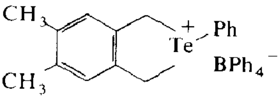
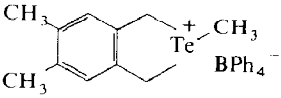
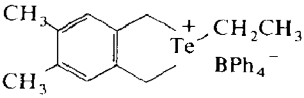
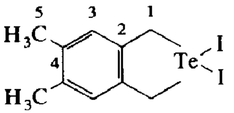
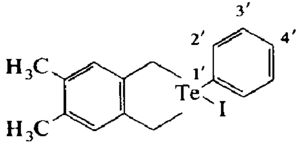
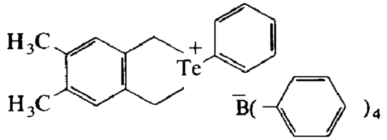
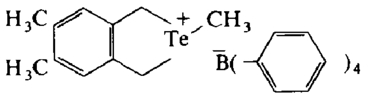
Compound		Chemical shifts (ppm); TMS = 0 ppm
	(I)	2.19 (CH_3, s, 6H); 4.70 (Te–CH_2, s, 4H); 7.05 (Ar–H, s, 2H)
	(II)	2.20 (CH_3, s, 6H); 4.23 (Te–CH_2, q, 4H, J(HH) 15.2 Hz); 7.08 (Ar–H, s, 2H); 7.38–7.53 (Ar–H, m, 3H); 7.65 (Ar–H, d, 2H)
	(III)	2.18 (CH_3, s, 6H); 4.38 (Te–CH_2, q, 4H), J(HH) 15.0 Hz); 6.93–7.60 (Ar–H, m, 22H)
	(IV)	1.98 (CH_3, s, 3H); 2.17 (CH_3, s, 6H); 4.00 (Te–CH_2, q, 4H, J(HH) 14.9 Hz); 6.75–7.16 (Ar–H, m, 22H)
	(V)	1.21 (CH_3, t, 3H); 2.06 (CH_2, q, 2H); 2.18 (CH_3, s, 6H); 4.05 (Te–CH_2, q, 4H, J(HH) 15.2 Hz); 7.16–7.74 (Ar–H, m, 22H)

Table 3

^{13}C NMR data for 5,6-dimethyl-1,3-dihydro-2-telluraindene derivatives

Compound		$\delta(^{13}C(1))$	$\delta(^{13}C(2))$	$\delta(^{13}C(3))$	$\delta(^{13}C(4))$	$\delta(^{13}C(5))$	Other $\delta(^{13}C)$
	(I)	47.70	135.1	129.7	136.9	18.73	–
	(II)	39.77	136.2	129.6	136.4	18.76	135.2('C(1)), 133.0('C(2)), 129.4('C(3)), 130.6('C(4))
	(III)	39.75	135.8	129.6	136.5	18.73	135.2('C(1)), 133.0('C(2)), 129.7('C(3)), 130.7('C(4)), (164.1, 135.6, 133.3, 121.2 (phenyl bonded to B))
	(IV)	33.82	136.5	129.9	136.5	18.75	4.93 (163.9, 135.3, 132.4, 122.7 (phenyl bonded to B))

data [4,5,13–16]. The ^{13}C NMR data for compounds I and II show no signals for carbon atoms attached to boron, such signals are observed for compounds containing the BPh_4^- ion as relatively small peaks at 164.1 (III) and 163.9 ppm (IV) (see Table 3).

The mass spectrum of II shows a peak at $m/e = 466$, based on ^{130}Te, showing the correct isotopic pattern for a tellurium containing fragment and corresponding to $C_{10}H_{12}Te(Ph)I^+$. The absence of molecular ions for compounds I, III, IV and V can be attributed either to pyrolytic decomposition, at the high temperature, or to ready fragmentation. The fragments corresponding with high m/e values can be regarded as direct fragments of the molecular ion (see Experimental). The fragmentation of the tetraphenylborate entity was also observed in the spectra of compounds III, IV and V, as can be seen from the data in the Experimental section.

Acknowledgment

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