

Synthesis, Characterization, and Solution Properties of New Heterocyclic Tellurium Compounds Based on 5,6-Dimethyl-1,3-dihydro-2-telluraindene

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ABSTRACT

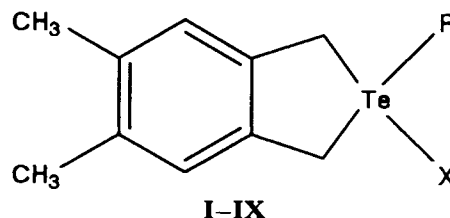
The synthesis and characterization of a new range of heterocyclic tellurium compounds based on 5,6-dimethyl-1,3-dihydro-2-telluraindene are reported. Conductivity measurements of most compounds in dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) showed considerable ionic character in both solvents. ^1H and ^{13}C NMR studies indicated that the telluronium salts are stable to reductive elimination and no reaction between solute and solvent was observed. Benzyl and allyl telluronium salts are exceptional. Infrared and mass spectral data are reported and discussed.

INTRODUCTION

McWhinnie et al. [1-3] showed that telluronium salts of the type $\text{Ph}_2\text{Te}(\text{CH}_3)\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{PhCOO}$) reductively eliminate CH_3X in solvents such as chloroform at a rate that was dependent on the anionic group, X. Some evidence for the involvement of a free radical was obtained from spin trapping experiments applied to both the reductive elimination and to oxidative addition of CH_3X to Ph_2Te [2]. Rainville and Zingaro [4] reported that the difference in the methyl ^1H NMR resonance of 10-methylphenoxatelluronium iodide in DMF-d_7 versus that in $(\text{CD}_3)_2\text{SO}$ is due to the formation of phenoxatellurine and $[(\text{CD}_3)_2\text{SOCH}_3]^+\text{I}^-$, and stated that this methylation and demethylation equilibrium is reversible for methyltelluronium salts [4].

Our previous works [5-9] demonstrated that heterocyclic telluronium salts of types $\text{C}_8\text{H}_{10}\text{Te}(\text{R})\text{X}$ [5], $\text{C}_4\text{H}_8\text{Te}(\text{R})\text{X}$ [6], $\text{C}_4\text{H}_8\text{OTe}(\text{R})\text{X}$ [7], and $\text{C}_5\text{H}_{10}\text{Te}(\text{R})\text{X}$ [8, 9] are stable to reductive elimination in CHCl_3 , DMSO, and DMF solutions. Furthermore, no reaction between telluronium salts and DMSO was observed [5-9].

In the present work we report the synthesis, solution properties, and some solid state data, which we required to obtain more information about the structure of compounds in solution, for the new range of heterocyclic tellurium compounds (I-IX). Some unexpected behavior is reported.



Ia: $\text{R} = \text{X} = \text{I}$; **Ib:** $\text{R} = \text{X} = \text{Br}$; **Ic:** $\text{R} = \text{X} = \text{Cl}$;
II: $\text{R} = \text{I}, \text{X} = \text{CH}_3\text{COO}$; **III:** $\text{R} = \text{X} = \text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$; **IVa:** $\text{R} = \text{CH}_3, \text{X} = \text{I}$; **IVb:** $\text{R} = \text{CH}_3, \text{X} = \text{Cl}$; **IVc:** $\text{R} = \text{CH}_3, \text{X} = \text{NCS}$; **IVd:** $\text{R} = \text{CH}_3, \text{X} = \text{OSO}_3\text{CH}_3$; **IVe:** $\text{R} = \text{CH}_3, \text{X} = \text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$; **IVf:** $\text{R} = \text{CH}_3, \text{X} = \text{BPh}_4$; **Va:** $\text{R} = \text{C}_2\text{H}_5, \text{X} = \text{I}$; **Vb:** $\text{R} = \text{C}_2\text{H}_5, \text{X} = \text{Br}$; **Vc:** $\text{R} = \text{C}_2\text{H}_5, \text{X} = \text{BPh}_4$; **VIa:** $\text{R} = \text{CH}_2\text{CH}=\text{CH}_2, \text{X} = \text{Br}$; **VIb:** $\text{R} = \text{CH}_2\text{CH}=\text{CH}_2, \text{X} = \text{Cl}$; **VIIa:** $\text{R} = \text{CH}_2\text{Ph}, \text{X} = \text{Cl}$; **VIIb:** $\text{R} = 2,6(\text{Cl})_2\text{C}_6\text{H}_3\text{CH}_2, \text{X} = \text{Br}$; **VIII:** $\text{R} = p\text{-Br-C}_6\text{H}_4\text{CO-CH}_2, \text{X} = \text{Br}$; **IX:** $\text{R} = \text{C}_4\text{H}_4\text{NO}_2, \text{X} = \text{Br}$

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EXPERIMENTAL

Synthesis

2,2-Diiodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (Ia). This compound was prepared by following the literature [10, 11]. The product was recrystallized from DMF, mp 202–204°C (Lit. [10, 11] 204–205°C). Anal. Calcd. for $C_{10}H_{12}TeI_2$: C, 23.4; H, 2.50. Found: C, 23.1; H, 1.97.

5,6-Dimethyl-1,3-dihydro-2-telluraindene. A mixture of $C_{10}H_{12}TeI_2$ (5.13 g; 10 mmol) and sodium sulfide (4.40 g; 40 mmol) in 100 cm³ of water was heated with stirring in a boiling water bath for 30 min. The resulting mixture was diluted with ice water, and the precipitate of 5,6-dimethyl-1,3-dihydro-2-telluraindene was filtered off, washed with water, and recrystallized from petroleum ether (80–100°). The yellow flakes, which melted at 91°C, were obtained quantitatively (Lit. [12] 90–92°C). Anal. Calcd. for $C_{10}H_{12}Te$: C, 46.2; H, 4.66. Found: C, 46.1; H, 4.28.

2,2-Dibromo-5,6-dimethyl-1,3-dihydro-2-telluraindene (Ib). Excess of bromine in CCl_4 was mixed with a carbon tetrachloride solution of $C_{10}H_{12}Te$ and the resulting solution was stirred for 1 h. The pale yellow precipitate of compound **Ib** was filtered off, washed with CCl_4 , recrystallized from ethanol, and dried in vacuo, mp 238–240°C. Anal. Calcd. for $C_{10}H_{12}TeBr_2$: C, 28.6; H, 2.88. Found: C, 28.6; H, 2.84.

2,2-Dichloro-5,6-dimethyl-1,3-dihydro-2-telluraindene (Ic). 5,6-Dimethyl-1,3-dihydro-2-telluraindene was dissolved in diethyl ether and Cl_2 gas was bubbled through it for a few minutes. The white precipitate of compound **Ic** was filtered off, washed with ether, and dried. Recrystallization from ethanol afforded the white crystals of mp 232–234°C. Anal. Calcd. for $C_{10}Te_2Cl_2$: C, 34.4; H, 4.04. Found: C, 34.8; H, 3.63.

2-Iodo-2-acetato-5,6-dimethyl-1,3-dihydro-2-telluraindene (II). 2,2-Diiodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (1.29 g; 2.5 mmol) was treated with silver acetate (0.42 g; 2.5 mmol) in methanol (50 cm³). The mixture was initially stirred at room temperature for 1 h, then heated under reflux for 3 h. The solution was filtered hot to remove silver iodide and the filtrate was allowed to evaporate slowly. The white product was collected and recrystallized from methanol, mp 110–111°C. Anal. Calcd. for $C_{12}H_{15}O_2TeI$: C, 32.3; H, 3.39. Found: C, 32.0; H, 3.29.

2,2-Bis(diethyldithiocarbamate)-5,6-dimethyl-1,3-dihydro-2-telluraindene (III). To a solution of compound **Ia** (5.13 g; 10 mmol) in dichloromethane (50 cm³) was added with stirring a solution of sodium diethyldithiocarbamate (3.5 g; 21 mmol) in dry

ethanol (50 cm³) at room temperature. The residue was treated with dichloromethane (20 cm³) and filtered to remove sodium iodide. Removal of dichloromethane and recrystallization from methanol gave the white crystals, mp 136–138°C. Anal. Calcd. for $C_{20}H_{32}N_2S_4Te$: C, 43.2; H, 5.79; N, 5.03. Found: C, 43.1; H, 5.81; N, 5.08.

2-Iodo-2,5,6-trimethyl-1,3-dihydro-2-telluraindene (IVa). Excess of freshly distilled iodomethane (15 cm³) together with 5,6-dimethyl-1,3-dihydro-2-telluraindene (2.60 g; 10 mmol) was placed in a flask flushed with dry nitrogen. An exothermic reaction took place giving a white precipitate that on recrystallization from ethanol/water (4/1) gave white crystals of mp 193°C. Anal. Calcd. for $C_{11}H_{15}TeI$: C, 32.9; H, 3.76. Found: C, 32.9; H, 3.84.

The following compounds were then prepared by oxidative addition of the appropriate organic halide to the cyclic telluride under the previous conditions.

2-Ethyl-2-iodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (Va). White crystals, mp 162–164°C. Anal. Calcd. for $C_{12}H_{17}TeI$: C, 34.7; H, 4.12. Found: C, 34.7; H, 4.18.

2-Ethyl-2-bromo-5,6-dimethyl-1,3-dihydro-2-telluraindene (Vb). White crystals, mp 184–186°C. Anal. Calcd. for $C_{12}H_{17}TeBr$: C, 38.98; H, 4.63. Found: C, 38.9; H, 4.59.

2-Allyl-2-bromo-5,6-dimethyl-1,3-dihydro-2-telluraindene (VIa). White crystals, mp 190–192°C. Anal. Calcd. for $C_{13}H_{17}TeBr$: C, 46.4; H, 4.50. Found: C, 46.9; H, 4.26.

2-Allyl-2-chloro-5,6-dimethyl-1,3-dihydro-2-telluraindene (VIb). White crystals, mp 180–182°C. Anal. Calcd. for $C_{13}H_{17}TeCl$: C, 46.4; H, 5.09. Found: C, 46.2; H, 5.19.

2-Benzyl-2-chloro-5,6-dimethyl-1,3-dihydro-2-telluraindene (VIIa). White crystals, mp 185°C. Anal. Calcd. for $C_{17}H_{19}TeCl$: C, 52.8; H, 4.96. Found: C, 52.7; H, 4.82.

2-(2,6-Dichlorobenzyl)-2-bromo-5,6-dimethyl-1,3-dihydro-2-telluraindene (VIIb). An ethereal solution of 2,6-dichlorobenzyl bromide (1.68 g; 6 mmol) was added to an ethereal solution of 5,6-dimethyl-1,3-dihydro-2-telluraindene (1.56 g; 6 mmol) to afford a crude white precipitate of compound **VIIb**. One recrystallization from ethanol gave white crystals, mp 144–146°C. Anal. Calcd. for $C_{17}H_{17}BrCl_2Te$: C, 40.9; H, 3.45. Found: C, 41.2; H, 3.56.

2-(p-Bromophenacyl)-2-bromo-5,6-dimethyl-1,3-dihydro-2-telluraindene (VIII). 5,6-Dimethyl-1,3-dihydro-2-telluraindene (2.60 g; 10 mmol) and

p-bromophenacyl bromide (2.78 g; 10 mmol) were mixed and sufficient diethyl ether was added to dissolve the reactants. The flask was stoppered and left overnight. The white precipitate was filtered off, washed with ether, and dried over P₄O₁₀. Recrystallization from ethanol/water (3/1) gave white crystals, mp 183°C. Anal. Calcd. for C₁₈H₁₈Br₂O₂Te: C, 40.2; H, 3.37. Found: C, 39.9; H, 3.28.

2-Succinimido-2-bromo-5,6-dimethyl-1,3-dihydro-2-telluraindene (IX). To a solution of 5,6-dimethyl-1,3-dihydro-2-telluraindene (1.56 g; 6 mmol) in 30 cm³ of benzene was added a solution of *N*-bromosuccinimide (1.06 g; 6 mmol) in 30 cm³ of benzene. The resulting mixture was filtered, and white crystals of compound **IX** were collected and washed with benzene. Recrystallization from ethanol gave white crystals, mp 140–142°C. Anal. Calcd. for C₁₄H₁₆BrNO₂Te: C, 38.5; H, 3.69. Found: C, 38.7; H, 3.72.

2-Chloro-2,5,6-trimethyl-1,3-dihydro-2-telluraindene (IVb). Compound **IVa**, C₁₀H₁₂Te(CH₃)₃I, (1.61 g; 4 mmol) dissolved in hot methanol (50 cm³) was added to an aqueous solution of silver chloride (0.57 g; 4 mmol). The solution was refluxed for 4 h and filtered hot to remove silver iodide. The filtrate was allowed to evaporate slowly. The white solid was collected and recrystallized from methanol, mp 204–206°C. Anal. Calcd. for C₁₁H₁₅TeI: C, 41.4; H, 5.01. Found: C, 41.6; H, 4.96.

2-Thiocyanato-2,5,6-trimethyl-1,3-dihydro-2-telluraindene (IVc). A solution of compound **IVa** (0.803 g; 2 mmol) in 40 cm³ of methanol was added to an aqueous solution of silver thiocyanate (0.33 g; 2 mmol). The reaction mixture was stirred at room temperature for 1 h, then refluxed for 4 h. The solution was filtered hot to remove silver iodide. The filtrate was allowed to evaporate at room temperature. The white crystals were collected. One recrystallization from methanol gave white crystals, mp 120–122°C. Anal. Calcd. for C₁₂H₁₅NSTe: C, 43.3; H, 4.45; N, 4.20. Found: C, 42.8; H, 4.64; N, 4.22.

2-Methylsulfato-2,5,6-trimethyl-1,3-dihydro-2-telluraindene (IVd). Excess of dimethyl sulfate (15 cm³) was added to 5,6-dimethyl-1,3-dihydro-2-telluraindene (0.77 g; 3 mmol). An exothermic reaction took place giving white precipitates. One recrystallization from methanol gave white crystals that melted at 129°C. Anal. Calcd. for C₁₂H₁₈O₄STe: C, 35.7; H, 4.95. Found: C, 35.7; H, 4.59.

2-Diethyldithiocarbamate-2,5,6-trimethyl-1,3-dihydro-2-telluraindene (IVe). To a solution of compound **IVa** (1.21 g; 3 mmol) in dichloromethane (30 cm³) was added with stirring under nitrogen a solution of sodium diethyldithiocarbamate (1.06 g; 6 mmol) in methanol (20 cm³) at room temperature.

The stirring was continued for 1 h after which the solvents were removed on a rotary evaporator. The product was treated with dichloromethane and filtered to remove sodium iodide. Removal of solvent and recrystallization from methanol gave a white precipitate that melted at 136–138°C. Anal. Calcd. for C₁₆H₂₅NS₂Te: C, 37.6; H, 4.64; N, 1.63. Found: C, 37.0; H, 4.58; N, 1.43.

Compounds 2,5,6-trimethyl-1,3-dihydro-2-telluraindene tetraphenylborate (**IVf**) and 2-ethyl-5,6-dimethyl-1,3-dihydro-2-telluraindene tetraphenylborate (**Vc**) were prepared as previously described [10, 11].

Physical Measurements

Infrared spectra (KBr discs) were recorded in the range 4000–200 cm⁻¹ on a Pye-Unicam SP3-300s spectrophotometer. Conductivity measurements were carried out by WTW conductivity meter LBR, using a standard cell with cell constant of 1.0850. ¹H NMR spectra were recorded on a Bruker MW-250 MHz with TMS as the internal reference. ¹³C NMR spectra were recorded on a Bruker AC-250 spectrophotometer at 61.9 MHz with TMS as the internal reference. Mass spectra were measured at 70 eV with an MAT 1125 Finnigan mass spectrometer; peaks shown relate to ¹³⁰Te, ¹¹B, ⁸¹Br, ¹H, and ¹²C.

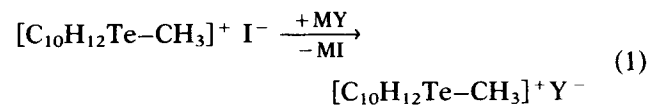
Microanalyses for carbon, hydrogen, and nitrogen were performed at Micro Analytical Service of Fakultät für Chemie, Universität Konstanz, F.R.G. Melting points were determined with a Gallenkamp apparatus and are uncorrected.

RESULTS AND DISCUSSION

In the presence of sodium iodide, 1,2-bis(chloromethyl)-4,5-dimethylbenzene reacted with elemental tellurium in 2-butoxyethanol to form 2,2-diiodo-5,6-dimethyl-1,3-dihydro-2-telluraindene (**Ia**) in a quantitative yield. Reduction of **Ia** with hydrated sodium sulfide yielded 5,6-dimethyl-1,3-dihydro-2-telluraindene. This compound (i.e. C₁₀H₁₂Te) can be easily oxidized to the corresponding dihalo and telluronium compounds with the appropriate dihalogens and alkyl halides respectively.

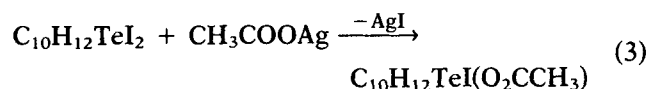
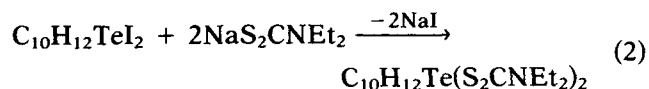
The preparation of compound **IVd**, using dimethyl sulfate as alkylating agent, gave the pure compound in almost quantitative yield.

Anion exchange reactions using 2-iodo-2,5,6-trimethyl-1,3-dihydro-2-telluraindene (**IVa**) as a starting material produced several new methylated telluronium salts (Equation 1).

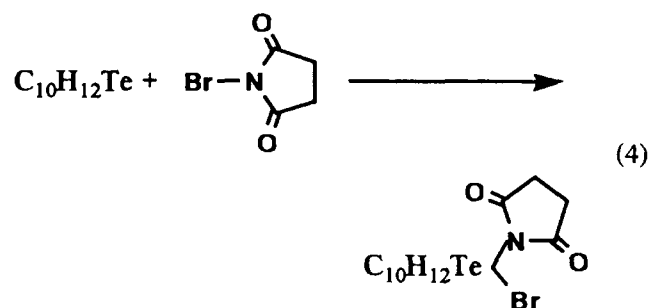


MY: AgCl; AgSCN; NaS₂N(C₂H₅)₂; NaBPh₄

This halogen exchange reaction was extended to compound **Ia**, as shown in Equations 2 and 3.



It was found that 5,6-dimethyl-1,3-dihydro-2-telluraindene can readily insert the *N*-bromine bond of *N*-bromosuccinimide (Equation 4), as reported for the reaction of diaryltelluride with *N*-bromosuccinimide [13].

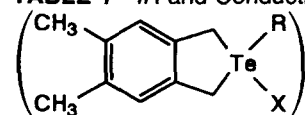


All reactions are, in general, essentially quantitative and yielded pure compounds after one recrystallization.

The molar conductance of each compound was measured in DMSO and DMF. All compounds, except compound **III**, gave appreciable conducting solutions at a concentration of 10^{-3} M (Table 1). The plots of molar conductance (Λ_M) against concentration^{1/2} are typical of weak electrolytes. Thus it would appear that there is some degree of ion-pairing in both solvents. These observations agree well with those of the previous work [1–3, 5–9]. The electrolytic nature of compound **IVe** and non-conducting behavior of compound **III** may be due to the electronic effect of a methyl group covalently attached to the tellurium atom. Compounds **Ib**, **Ic**, **II**, and **IX** had low conductivities in DMSO and DMF (Table 1); this may be due to the association of these compounds via ionic bonds in both solvents, since it is well known from crystallographic studies that association of organotellurium compounds is common [14–17].

Compounds **IVf** and **Vc** give a low conductivity in DMSO and DMF (Table 1). This may be attributed to the close contact between a tellurium atom and one phenyl ring of the tetraphenylborate anion

TABLE 1 IR and Conductivity Data for 5,6-Dimethyl-1,3-dihydro-2-telluraindene Derivatives



Compound	Molar Conductivity (Λ_M) ^a		IR Data (cm^{-1})	
	DMSO*	DMF*	$\nu(\text{Te}-\text{R})$	Other Bands
Ia	36.6	54.7		3010w, 2965m, 2910w, 1612m.
Ib	19.5	27.6		3010w, 2965m, 2920w, 1610m.
Ic	15.3	23.3		3010w, 2960m, 2920w, 1612m, 346s.
II	19.6	28.2		3010w, 2965w, 2920w, 1720s, 1610m.
III	1.8	3.2		3020w, 2965w, 2916w–m, 1610w, 1482s, 985m, 322w–m.
IVa	31.5	52.1	530w	3005w, 2916w, 1610w–m.
IVb	29.6	60.6	538w	3020w, 2900w, 1610m.
IVc	28.3	—	535w	3010w, 2918w, 2040s, 1610m, 975m–s.
IVd	28.6	53.5	535w	3008w, 2924w, 1612m.
IVe	21.8	48.2	540w	3010w, 2920w, 1615m, 1482s, 985s.
IVf	15.6	33.7	535w	3010w, 2924w, 1612w–m.
Va	35.8	61.3	538w	3015w, 2914w, 1612m.
Vb	30.1	56.7	540w	3010w, 2920w, 1618m.
Vc	17.3	34.5	540w	3010w, 2920w, 1614m.
Vla	28.3	55.6	540w	3020w, 2920w, 1618w.
Vlb	27.7	34.3	540w	3010w, 2918w, 1612m.
VIIa	19.0	46.3	535w	3010w, 2919w, 1612m.
VIIb	21.8	37.7	538w	3020w, 2925w, 1610m.
VIII	21.6	37.7	538w	3020w, 2925w, 1655s, ^b 1610m.
IX	25.2	47.2	535 ^c	3010w, 2920w, 1720s, ^b 1610m.

^a 10^{-3} M solutions: Et_4NCl $\Lambda_M(\text{DMSO})$ 30; $\Lambda_M(\text{DMF})$ 80 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

^b $\nu(\text{CO})$.

^c $\nu(\text{Te}-\text{CH}_2)$.

* Graphic data may be obtained in ref. [11].

as shown by X-ray studies on analogous compounds [18].

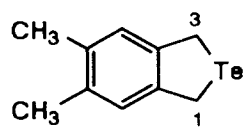
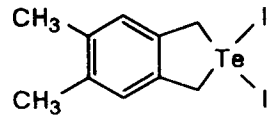
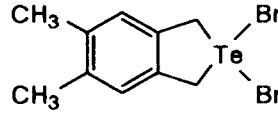
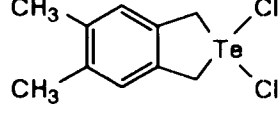
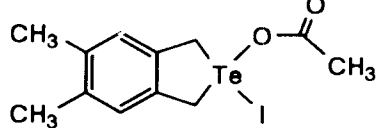
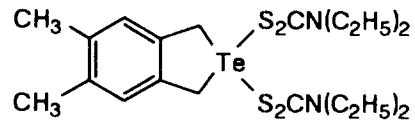
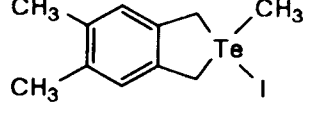
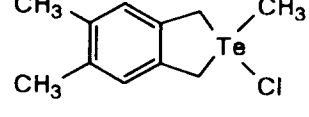
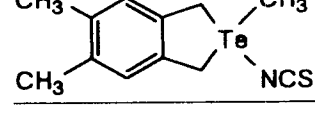
Some representative infrared spectra (KBr discs) for all compounds are given in Table 1. Generally, the infrared spectra of all compounds show $\nu(\text{Te}-\text{C}_{\text{alkyl}})$ bands between 530–540 cm^{-1} while the $\nu(\text{Te}-\text{C}_{\text{cyclic}})$ bands appear between 430–440 cm^{-1} .

The infrared spectra of compound **VIII** as a KBr disc and in chloroform solution are almost identical and show a band at 1655 cm^{-1} corresponding to $\nu(\text{C}=\text{O})$. The slight lowering of $\nu(\text{C}=\text{O})$ frequency

compared with that of *p*-bromoacetophenone (1660 cm^{-1}) may be due to the coordination of the carbonyl oxygen to the tellurium atom, in which the phenacyl group is acting as an unsymmetrical bidentate ligand [6]. The infrared spectrum of compound **VIII** in chloroform solution remained unchanged with time, providing good evidence for nonoccurrence of reductive eliminations [5–9].

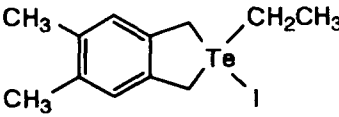
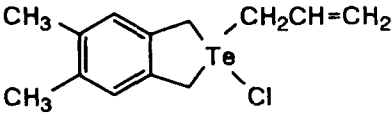
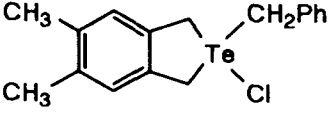
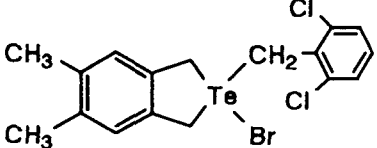
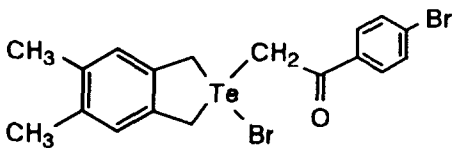
Infrared spectra of compounds **III** and **IVd** showed the characteristic frequencies for diethylthiocarbamate ligands [19–21] (see Table 1).

TABLE 2 Some ^1H NMR Data for 5,6-Dimethyl-1,3-dihydro-2-telluraindene Derivatives^a (Data for all compounds prepared are in ref. [11])

Compound	Chemical Shifts (ppm); TMS = 0 ppm
	2.14(CH ₃ , s, 6H); 4.38(Te-CH ₂ , s, 4H); 6.95(Ar-H, s, 2H).
	2.19(CH ₃ , s, 6H); 4.70(Te-CH ₂ , s, 4H); 7.05(Ar-H, s, 2H).
	2.19(CH ₃ , s, 6H); 4.64(Te-CH ₂ , s, 4H); 7.05(Ar-H, s, 2H).
	2.20(CH ₃ , s, 6H); 4.47(Te-CH ₂ , s, 4H); 7.05(Ar-H, s, 2H).
	2.13(CH ₃ + CH ₃ CO, s, 9H); 4.03(Te-CH ₂ , q, 4H, $J(\text{HH}) = 15.4$ Hz); 6.94(Ar-H, s, 2H).
	1.19(CH ₃ , t, 12H); 2.16(CH ₃ , s, 6H); 3.83(CH ₂ , q, 8H); 4.16(Te-CH ₂ , s, 4H); 6.97(Ar-H, s, 2H).
	1.93(CH ₃ , s, 6H); 2.18(CH ₃ , s, 3H); 4.02(Te-CH ₂ , q, 4H, $J(\text{HH}) = 14.9$ Hz); 6.95(Ar-H, s, 2H).
	1.93(CH ₃ , s, 6H); 2.19(CH ₃ , s, 3H); 4.04(Te-CH ₂ , q, 4H, $J(\text{HH}) = 15.0$ Hz); 6.96(Ar-H, s, 2H).
	1.93(CH ₃ , s, 6H); 2.18(CH ₃ , s, 3H); 4.04(Te-CH ₂ , q, 4H) $J(\text{HH}) = 15.0$ Hz); 6.95(Ar-H, s, 2H).

(continued)

TABLE 2 Some ^1H NMR Data for 5,6-Dimethyl-1,3-dihydro-2-telluraindene Derivatives^a (Data for all compounds prepared are in ref. [11]) (continued)

Compound	Chemical Shifts (ppm); TMS = 0 ppm
	1.22(CH ₃ , t, 3H); 2.07(CH ₂ , q, 2H); 2.18(CH ₃ , s, 3H); 4.05(Te-CH ₂ , q, 4H, $J(\text{HH}) = 15.08$ Hz); 6.97(Ar-H, s, 2H).
	2.14(CH ₃ , s, 6H); 4.15(CH ₂ , d, 2H); 4.19(q) + 4.36(s)(Te-CH ₂ , ca. 4H, $J(\text{HH}) = 15.3$ Hz); 4.93(CH ₂ , d, 2H); 5.04(CH, p, 1H); 6.96(Ar-H, s, 2H).
	2.14(CH ₃ , s, 6H); 3.95(q) + 4.36(s)(Te-CH ₂ , ca. 4H, $J(\text{HH}) = 15.3$ Hz); 4.75(CH ₂ , s, 2H); 6.96(Ar-H, s, 2H); 7.34(Ar-H, s, 5H).
	2.17(CH ₃ , s, 6H); 4.16(q) + 4.38(s)(Te-CH ₂ , ca. 4H, $J(\text{HH}) = 15.1$ Hz); 4.68(CH ₂ , s, 2H); 6.99(Ar-H, s, 2H); 7.25(Ar-H, d, 2H); 7.39(Ar-H, d, 2H).
	2.17(CH ₃ , s, 6H); 4.10(Te-CH ₂ , q, 4H, $J(\text{HH}) = 15.0$ Hz); 4.22(CH ₂ , s, 2H); 6.94(Ar-H, s, 2H); 7.72(Ar-H, s, 4H).

^a In DMSO-d₆.

The infrared spectrum of $[\text{C}_{10}\text{H}_{12}\text{Te}-\text{CH}_3]^+ \text{NCS}^-$ (**IVc**) is characterized by a sharp and strong band at 2040 cm^{-1} . Thus, we believe that the NCS group is bonded via nitrogen to the tellurium atom [1, 22].

Some representative ^1H NMR data, in DMSO-d₆, are collected in Table 2. The methylene protons (1 and 3, Table 2) give a singlet for 5,6-dimethyl-1,3-dihydro-2-telluraindene and for dihalo derivatives, and for compound **III**. However, formation of telluronium salts and of compound **II** changes the methylene spectrum to a simple AB pattern. This means that the two methylene protons (1 and 3, Table 2) are nonequivalent due to two different substituents on the tellurium atom. The coupling constant is ca. 15 Hz, a value consistent with an sp^3 hybridized carbon [5, 10, 23]. As can be seen from Table 2, the chemical shifts of methylene protons, for compounds **Ia–Ic**, depends on the size and electronegativity of the halogen attached covalently to the tellurium atom. In the case of telluronium salts, the change of counterion (Cl, Br, I, NCS, OSO_2Me , BPh_4) does not affect the chemical shifts of the methylene protons (1 and 3, Table 2). Thus we can interpret this result as proof of the ionic nature of the halogen–tellurium bonds (see Conductivity dis-

cussion). The value of $\delta(\text{CH}_3)$ is always around 1.93. This implies the same associated form, or the same solvated ionic form, of the telluronium cation in DMSO.

The initial spectrum of **IVa** or **Vb** was unchanged after 24 h, indicating the resistance of these compounds to reductive elimination behavior, consistent with that of salts derived from telluracyclopentane [5, 6, 9a] and telluracyclohexane [7, 8]. Surprisingly, the ^1H NMR spectra for allyl and benzyl derivatives (i.e. compounds **VIa**, **VIb**, **VIIa**, and **VIIb**) showed two separate signals for the methylene protons (1 and 3, Table 2), singlet at δ 4.36, and a quartet around δ 4.0 due to 5,6-dimethyl-1,3-dihydro-2-telluraindene and telluronium salts respectively. The sum of the intensities of singlet and quartet signals correspond to four protons (see Table 2). This indicates that these compounds tend to eliminate allyl and benzyl halides in DMSO solution. McWhinnie et al. [2] gave some evidence obtained from spin trapping experiments for the involvement of a free radical as applied to the reductive elimination and to the oxidative addition of CH_3X to Ph_2Te . Thus, it seems likely that the reductive elimination of allyl and benzyl halides occurred via a free radical mechanism, since it is

well known that allyl and benzyl groups form relatively stable free radicals. Such phenomena were not seen for compound **VIII**. This may be due to the coordination of the carbonyl oxygen to the tellurium atom (see IR discussion).

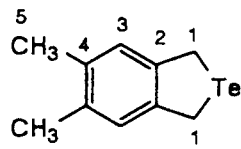
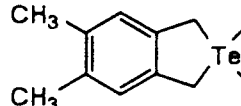
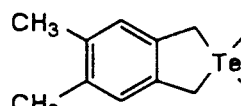
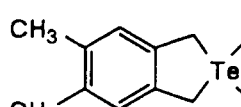
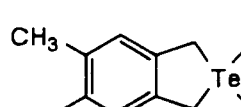
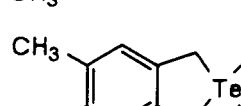
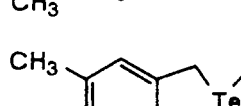
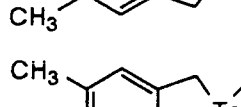
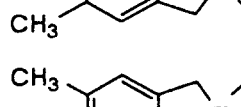
The ^{13}C NMR data were obtained in DMSO-d_6 (Table 3). The assignment of the signals of carbon atoms were made by the use of closely related organic and organotellurium compounds [5, 6, 17, 23, 24]. The large variation for carbon atoms bearing tellurium atoms can be attributed to the polarity of the Te–C bond [5, 6, 25]. The observed increase

in the chemical shifts of C-1 (Table 3) in going from compound **Ia** to **Ic** is due to the electronegativity of halogen attached covalently to the tellurium atom.

The ^{13}C spectra for compounds **VIa**, **VIb**, **VIIa**, and **VIIb** show some extra signals that may be attributed to the occurrence of the reductive elimination of these compounds (see Table 3).

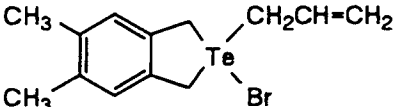
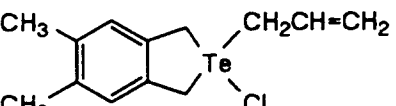
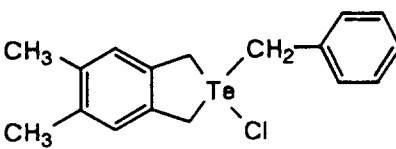
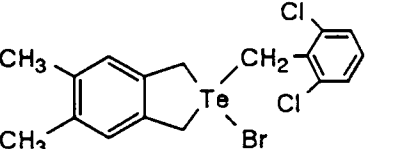
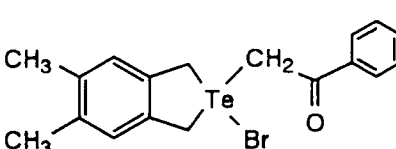
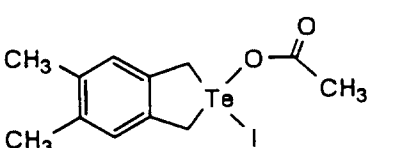
The mass spectra for all compounds were recorded at 70 eV. The spectra are in general closely related to those of cyclic telluronium salts [5, 6]. The absence of molecular ions, for all compounds, can be attributed either to pyrolytic decomposition,

TABLE 3 ^{13}C NMR Data for 5,6-Dimethyl-1,3-dihydro-2-telluraindene Derivatives^a

Compound	$\delta(^{13}\text{C}(1))$	$\delta(^{13}\text{C}(2))$	$\delta(^{13}\text{C}(3))$	$\delta(^{13}\text{C}(4))$	$\delta(^{13}\text{C}(5))$	Other $\delta(^{13}\text{C})^b$
	8.8	133.3	128.1	141.1	18.6	
	47.7	135.1	129.7	136.9	18.7	
	50.8	135.2	130.1	136.6	18.7	
	53.1	135.2	130.2	136.4	18.7	
	35.5	135.0	129.1	136.4	18.7	5.4
	35.3	134.9	130.0	137.0	18.7	8.6
	34.2	135.3	129.9	136.6	18.7	5.2, 128
	33.2	135.9	129.5	136.8	18.7	18.6, 9.8
	33.6	134.9	129.6	137.1	18.7	19.2, 9.8

(continued)

TABLE 3 ^{13}C NMR Data for 5,6-Dimethyl-1,3-dihydro-2-telluraindene Derivatives^a (continued)

Compound	$\delta(^{13}\text{C}(1))$	$\delta(^{13}\text{C}(2))$	$\delta(^{13}\text{C}(3))$	$\delta(^{13}\text{C}(4))$	$\delta(^{13}\text{C}(5))$	Other $\delta(^{13}\text{C})^b$
	35.1 8.6(?)	135.1 135.5(?)	129.6 128.1(?)	136.7 134.5(?)	18.9	29.5, 129.2, 120.2
	34.4 8.7(?)	134.8 134.3(?)	129.6 128.3(?)	137.0 137.1(?)	18.8	29.3, 129.2, 119.9
	31.4 8.6(?)	134.8 126.9(?)	129.4 128.0(?)	136.4 128.1(?)	18.8	35.6, 135.1, 129.2, 128.4, 127.8
	31.3 8.6(?)	135.1 134.9(?)	129.6 129.2(?)	136.0 136.7(?)	18.8 24.2(?)	37.0, 136.8, 134.6, 128.3, 129.6
	31.2	135.1	129.6	136.7	18.7	36.3, 193.8, 135.3, 130.1, 131.0, 129.7
	31.3	135.1	130.4	136.9	18.8	13.6, 205.2

^a Referred to internal TMS in ppm. DMSO- d_6 solvent.

^b Chemical shifts are given in increasing order C(1'), C(2') etc.

in direct inlet, at the high temperature that was used or to electron impact. Data and the probable fragmentation pattern are given in ref. [11].

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