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2-Methyl-1-organo-1-halo-1-telluracyclopentane: synthesis, solution properties, and configurational studies

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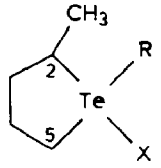
Abstract

Some new heterocyclic tellurium compounds containing the 2-methyl-1-organo-1-telluracyclopentane cation have been prepared. ^{1}H NMR studies show the presence of *cis / trans* geometrical isomers. The effect of organyl group and the anion on the *cis / trans* ratio have been investigated. All the compounds are stable towards reductive elimination and do not react with the solvent. The conductivities in dimethylsulphoxide (DMSO) and *N,N*-dimethylformamide (DMF) indicate that there is some ion pairing. IR and mass spectral data are reported and discussed.

Introduction

We recently described the synthesis and configurations of the first 2-methyl-1-organo-1-halo-1-telluracyclopentane [1], and noted the presence of a mixture of *cis / trans* geometrical isomers with the *trans*-isomer as a major product. The isomer ratio was found to be greatly affected by the size of the alkyl group attached covelently to the tellurium atom [1]. Thermogravimetric analysis [2] showed that the decomposition of 1,2-dimethyl-1-iodo-1-telluracyclopentane proceeded in three stages, and that 2-methyl-1,1-diiodo-1-telluracyclopentane vaporised at 165 °C.

We describe here the synthesis of a new range of cyclic telluronium salts derived from 2-methyl-1-telluracyclopentane (I–VI). The effect of the size of organic group and the anion on *cis / trans* ratio has been investigated by means of ^{1}H NMR spectroscopy. The solution properties and some solid data for these compounds are also described.



(I-VI)

(Ia: R = CH_3, X = Cl; Ib: R = CH_3, X = I; Ic: R = CH_3, X = BPh_4; IIa: R = CH_3CH_2, X = I; IIb: R = CH_3CH_2, X = BPh_4; IIIa: R = CH_2=$CHCH_2$, X = Br; IIIb: R = CH_2=$CHCH_2$, X = I; IV: R = $C_6H_5CH_2$, X = Br; V: R = C_6H_5, X = BPh_4; VIa: R = Cl, X = Cl; VIb: R = Br, X = Br; VIc: R = I, X = I)

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Experimental

(a) Synthesis

Compounds Ib, IIa, IV and VIc were prepared as previously reported [1].

2-Methyl-1-allyl-1-bromo-1-telluracyclopentane (IIIa). Sodium borohydride was added to a boiling methanol solution of 2-methyl-1,1-diiodo-1-telluracyclopentane (2.0 g) until the orange colour disappeared. The solution was filtered, then poured into 1 l of water. After extraction with ether (3 × 100 ml), the extracts were dried over anhydrous magnesium sulphate and the solvent removed on a rotary evaporator. An excess of freshly distilled allyl-bromide (10 ml) was added to the residue, and the flask then stoppered and left overnight. The resulting white solid was washed with ether and dried over P_4O_{10}. One recrystallization from ethanol gave white crystals, m.p. 140–142 °C.

Found: C, 30.23; H, 4.66; Te, 41.40. $C_8H_{15}TeBr$ calc: C, 30.27; H, 4.66; Te, 40.00%.

2-Methyl-1-allyl-1-iodo-1-telluracyclopentane (IIIb). This compound was prepared similarly. The pale yellow solid formed was recrystallized from ethanol to give white crystals, m.p. 155–156 °C.

Found: C, 26.28; H, 4.27; Te, 34.60. $C_8H_{15}TeI$ calc: C, 26.27; H, 4.27; Te, 34.89%.

1,2-Dimethyl-1-chloro-1-telluracyclopentane (Ia). An aqueous solution of silver chloride (2.0 g, 0.01 mol) was added to an ethanolic solution of 1,2-dimethyl-1-iodo-1-telluracyclopentane (2.7 g, 0.01 mol). The solution was heated under reflux for 2 h, then filtered hot, and the filtrate reduced to dryness. One recrystallization from ethanol gave white crystals, m.p. 175–176 °C.

Found: C, 28.96; H, 5.25; Te, 50.01. $C_6H_{11}TeCl$ calc: C, 29.03; H, 5.28; Te, 51.14%.

For the preparations of compounds Ic and IIb, a mixture of the 2-methyl-1-organo-1-iodo-1-telluracyclopentane (0.01 mol) and sodium tetraphenylborate (3.42 g, 0.01 mol) in dry ethanol (100 ml) was stirred for 2 h, then heated under reflux for 15 min. The white precipitate was filtered off recrystallized from 1/3 DMF/water.

1,2-Dimethyl-1-telluracyclopentane tetraphenylborate (Ic). This compound melted at 227 °C.

Found: C, 67.15; H, 5.80; Te, 22.75. $C_{30}H_{33}TeB$ calc: C, 67.73; H, 6.25; Te, 23.98%.

2-Methyl-1-ethyl-1-telluracyclopentane tetraphenylborate (IIb). This compound melted at 241–243 °C.

Found: C, 69.06; H, 6.05; Te, 22.10. $C_{31}H_{35}TeB$ calc: C, 69.19; H, 6.46; Te, 23.40%.

2-Methyl-1-phenyl-1-telluracyclopentane tetraphenylborate (V). A mixture of 2-methyl-1,1-diiodo-1-telluracyclopentane (4.52 g, 0.01 mol) and sodium tetraphenylborate (6.84 g, 0.02 mol) in dry ethanol (100 ml) was stirred for 2 h under reflux then filtered hot. The white crystals were collected, washed with water then with ethanol, and recrystallized from DMF/water as white crystals, m.p. 208 °C.

Found: C, 69.91; H, 5.35; Te, 20.10. $C_{36}H_{39}TeB$ calc: C, 70.76; H, 5.93; Te, 21.40%.

2-Methyl-1,1-dibromo-telluracyclopentane (VIb). A solution of bromine (1.44 g, 0.009 mol) in 50 ml of ether was added dropwise to a solution of 2-methyl-1-tel-

luracyclopentane (1.58 g, 0.008 mol) in 100 ml of ether. A pale yellow precipitate was formed immediately. The solution was evaporated to dryness and residue recrystallized from ethanol to give white crystals, m.p. 176–178° C.

Found: C, 16.97; H, 2.79; Te, 34.80. $C_5H_{10}TeBr$ calc: C, 16.79; H, 2.82; Te, 35.68%.

2-Methyl-1,1-dichloro-1-telluracyclopentane (VIa). This compound was prepared analogously by reaction with SO_2Cl_2. The product was obtained as white crystals after recrystallization from ethanol, m.p. 186–188° C.

Found: C, 21.85; H, 3.30; Te, 46.20. $C_5H_{10}TeCl_2$ calc: C, 22.36; H, 3.75; Te, 47.50%.

(b) Physical measurements

^1H NMR spectra were recorded on a Bruker WH-90 DC spectrometer with TMS as internal reference. Solution conductivities were measured with a WTW conductivity meter LBR, using a standard conductivity cell with cell constant of 0.0577. Infrared spectra were recorded with KBr discs in the range 4000–200 cm^{-1} on a Beckman TM spectrophotometer. Microanalysis for carbon and hydrogen were carried out by Microanalytical Laboratories of the Chemistry Department of College of Science, University of Mosul. Tellurium analysis was carried out as described by Thavornyutikarn [3] by use of a Pye Unicam Spy flameless atomic absorption spectrometer. Melting points were determined on a Frost melting point apparatus and are uncorrected.

Results and discussion

The molar conductivity of each compound was determined for DMSO and DMF solutions. The results for single concentration (10^{-3} M) are presented in Table 1. The conductivity of each compound was studied as a function of the concentration in both solvents. In all cases appreciable ion pairing was noted, but in DMSO at least the values of Λ_M approach those expected for 1 : 1 electrolytes [5–8].

Table 1

Conductivity data (10^{-3} M solution) for 2-methyl-1-telluracyclopentane derivatives, $2\text{-}MeC_4H_7TeRX$

R	X	Λ_M(DMSO) [a] ($ohm^{-1}\,cm^2\,mol^{-1}$)	Λ_M (DMF) [a] ($ohm^{-1}\,cm^2\,mol^{-1}$)
CH_3	Cl	30.58	60.58
CH_3	I	27.69	54.80
CH_3	BPh_4	25.01	52.61
CH_3CH_2	I	26.60	47.89
$CH_2{=}CHCH_2$	Br	30.04	56.50
$CH_2{=}CHCH_2$	I	28.27	53.66
$C_6H_5CH_2$	Br	18.46	35.46
C_6H_5	BPh_4	24.81	46.16
Cl	Cl	9.60	10.38
Br	Br	16.30	17.40
I	I	18.30	19.61

[a] $[(C_2H_5)_4N]Cl$: Λ_M 30 (DMSO) 80 (DMF) $ohm^{-1}\,cm^2\,mol^{-1}$.

Table 2

Selected ^{1}H NMR data for 2-methyl-1-telluracyclopentane derivatives

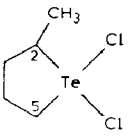
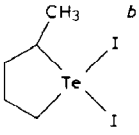
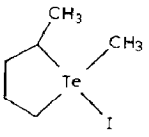
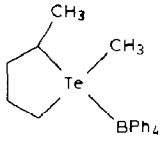
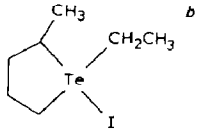
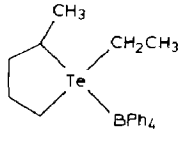
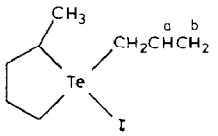
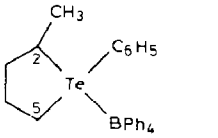
Compound	Solvent	Chemical shifts (ppm) [a] and assignment		*cis*/*trans* ratio
	DMSO-d_6	1.75 (d) 2.00–2.23(m) 2.52–3.18(m) 3.42–4.45(m) 3.42–4.20(m)	C^2-CH_3 H(3) H(4) H(2) H(5)	0/100
	DMSO-d_6	1.90(d) 2.20–2.55(m) 2.85–3.20(m) 3.80–4.45(m) 3.80–4.45(m)	C^2-CH_3 H(3) H(4) H(2) H(5)	0/100
	DMSO-d_6 [b]	1.45(d) 1.60(d) 2.10(s) 2.20(s) 1.80–2.75(m) 2.95–3.15 3.60–3.90(m)	C^2-CH_3 *cis* C^2-CH_3 *trans* Te-CH_3 *cis* Te-CH_3 *trans* H(3,4) H(5) H(2)	39/61
	$CDCl_3$	1.65(d) 1.92(d) 2.38(s) 2.52(s) 1.98–2.65(m) 2.95–3.20(m) 3.50–3.80(m)	C^2-CH_3 *cis* C^2-CH_3 *trans* Te-CH_3 *cis* Te-CH_3 *trans* H(3,4) H(5) H(2)	39/61
	DMSO-d_6	1.33(d) 1.47(d) 1.90(s) 2.20(s) 2.04–2.52(m) 2.66–3.09(m) 3.28–3.70(m)	C^2-CH_3 *cis* C^2-CH_3 *trans* Te-CH_3 *cis* Te-CH_3 *trans* H(3,4) H(5) H(2)	35/65
	DMSO-d_6	1.95(d) 1.55–1.75(m) 2.35–2.65(m) 3.25(q)	C^2-Me *trans* *cis* C^2-Me + CH_2-CH_3 H(3,4) CH_2CH_3	ca. 27/73
	DMSO-d_6	1.15–1.34(m) 1.48(d) 1.61–2.31(m) 2.35–2.68(m) 2.86(q) 3.23–3.65(m) 6.61–7.21(m)	*cis* C^2-Me + CH_2CH_3 C^2-Me *trans* H(3,4) H(5) CH_2CH_3 H(2) Ar-H	ca. 25/75

Table 2 (continued)

Compound	Solvent	Chemical shifts (ppm) [a] and assignment		*cis/trans* ratio
	DMSO-d_6	1.56(d)	C^2-Me *trans*	0/100
		1.65–2.31(m)	H(3,4)	
		2.69–3.11(m)	H(5) + Te-CH_2	
		3.40–3.68(m)	H(2)	
		5.05–5.52(m)	H(a)	
		5.71–6.28(m)	H(b)	
	DMSO-d_6	1.80(d)	C^2-Me *trans*	0/100
		1.85–2.10(m)	H(3,4)	
		2.50–3.10(m)	H(5)	
		3.60–3.90(m)	H(2)	
		6.80–8.10(m)	Ar-H	

[a] Peak assignments are based on integrations, multiplicity, and structure, taking account of the downfield shift for the *trans* form [1,18]. [b] Data from ref. 1

Low conductivities in DMF have been also observed by other workers [6,7,9]. It thus appears that the compounds are extensively associated in DMF solution. Compounds VIa, VIb and VIc had low conductivities in DMSO and DMF (Table 1), this may be due to the association of these compounds via weak ionic bonds in both solvents, since it is well known from crystallographic studies that association of organotellurium(IV) dihalides is common [10–13].

The ^{1}H NMR spectra of 2-MeC_4H_7TeRX show the presence of *cis/trans* geometrical isomers, where R = CH_3 and CH_3CH_2, with the *trans*-configuration dominant. The isomer ratio was found to be greatly affected by the size of the organic group covalently attached to tellurium atom, as we observed previously [1]; thus, when the methyl or ethyl group is replaced by an allyl, benzyl, or phenyl group only the *trans*-isomer is present (Table 2).

In order to examine the effect of the size of the counter anion on the isomer ratio, we replaced the counter ion (Cl, Br, I) by the bulky tetraphenylborate ion. For X = BPh_4 (compounds I and IIb), the spectra showed the presence of both *cis* and *trans* isomers in each case. Integration of the signals from the above compounds indicated *cis/trans* ratios of 35/65 and ca. 27/75, respectively (compare the values for compounds Ia, Ib and IIa in Table 2). Thus the presence of the teraphenylborate anion had only a weak effect on the isomer ratio, and this may be attributed to the absence of the secondary interaction between the tetraphenylborate anion and the tellurium cation, as shown by crystallographic studies on organotellurium(IV) tetraphenylborate compounds [14,15].

The ^{1}H NMR spectrum of compound Ib was recorded immediately after a solution had been made up in DMSO-d_6. The positions of methyl resonances did not vary during 24 h. Similar behaviour was observed for the other salts (I–V). This indicates the stability of these compounds towards reductive elimination [6,7], as found for telluronium salts derived from telluracyclopentane [4,5] and oxatellurine [8]. There was no chemical reaction between the solute and DMSO of the type observed for other telluronium salts [16]. The ^{1}H NMR data for compound Ib show that the deshielding of the methyl protons is larger in $CDCl_3$ than in DMSO, this is a consequence of the superior solvating power of DMSO.

Table 3

Some IR data for 2-methyl-1-telluracyclopentane derivatives: 2-MeC_4H_7TeRX (KBr disc)

Ia	Ib	Ic	IIa	IIb	IIIa	IIIb	IV	V	VI	VIb	Assignments
–	–	3040m	–	3040m	–	–	3060m	3035m	–	–	aromatic C–H stretching
2870m	2870m	2870m	2870m	2890m	2870m	2875m	2875s	2870m	2870m	2870m	aliphatic C–H stretching
1320s	1320s	1480s	1320s	1489s	1455m	1455m	1460m	1480m	1380m	1350w	C–H bending
–	–	1480	–	1480	1630w	1635w	1455m	1450m	–	–	ν(C=C)
		1430		1430			1430m	1438m			
1210m	1215m	1238m	1205m	1240m	1228s	1230s	1242m	1235s	1240s	1235m	Symm. CH_3 vib.
1185s	1190m	1185m	1185s	1185s	1190s	1190s	1195m	1185m	1185m	1185m	CH_3 deformation.
850m	855m	855m	870m	852s	870m	875m	870m	850m	870m	870m	CH_3 rock.
525w	530w	505w	515w	528w	505w	510w	515w	255w [a]		–	ν(Te–C_{alkyl})
470w	475w	470w	475w	465m	485w	485w	485w	470w	485w	465w	ν(Te–$C^{2,5}$)
–	–	850		852	–	–	870w	850w	–	–	g(phenyl)
		750		740			765w	750w			
–	–	710s		710s	–	–	710s	710m	–	–	f(phenyl)
–	–	685m		630m			685m	630m	–	–	v(phenyl)
–	–	628		628	–	–	628w	–	–	–	r(phenyl)
		465		455							

[a] For (Te–C_{phenyl}). Following the notation of Whiffen and Ellestad et al. [17].

IR spectral data for compounds I–VI are given in Table 3, and show no unusual features. The $\nu(Te–C_{alkyl})$ bands are found between 505 and 530 cm^{-1} and the $\nu(Te–C^{2,5})$ band between 465 and 485 cm^{-1}.

The mass spectrum of 2-$MeC_4H_7Te(CH_3)I$, was recorded. As for cyclic telluronium salts [5,6,4] the molecular ion (M^+) is present in low abundance, at low intensity. The base peaks (100%) are the telluride ion 2-$MeC_4H_7Te^+$ and RX^+. Other ions observed are; 2-$MeC_4H_7TeCH_3^+$, 2-$MeC_4H_7Te^+$, 2-$MeC_4H_7^+$, $C_4H_7^+$, $TeCH_2CH_2^+$, $TeCH_2^+$, and Te^+.

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