Journal of Organometallic Chemistry, 157 (1978) 405—411

ORGANOTELLURIUM DERIVATIVES

III *. SYNTHESIS OF ANIONIC COMPLEXES OF 1-TELLURACYCLOPENTANE(IV) 1/1 DIIODIDE

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(Received March 31st, 1978)

Summary

Complexes containing tetrahalotelluracyclopentane anions of the type $(R_4M)_2{}^+$-$[C_4H_8TeX_2X'_2]^{2-}$ (where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_7H_{15} or C_6H_5; M = N, P, As or Sb; X = Cl, Br, or I and X′ = I, Cl, Br, NCO, NCS, or N_3) have been synthesised, (i) by the interaction of 1-telluracyclopentane 1/1 diiodide with the corresponding tetraorganoammonium, -phosphonium, -arsonium, or -stibonium halides in nonaqueous solvents and (ii) via halogen exchange between complex anions and silver or alkali metal halides. The second method also yielded several pseudohalide and mixed halide-pseudohalide derivatives. The ionic nature of the new complex anions has been established by conductance and molecular weight measurements. NMR and IR spectra of some of the derivatives are discussed.

Introduction

Penta- and hexa-halotellurates(IV) have been known since 1900 [1—5]. Although the first complex anion containing Te—C bonds, $[(CH_3)_3Te]^+[(CH_3)TeX_4]^-$, was reported [6] as early as 1929, it is only recently that a few papers describing tetrahalomonoaryltellurates(IV) [7,8] and dihaloaryltellurates(II) [9] have appeared. We have recently reported preparation of aryltellurium chlorides by a cleavage reaction of M—Ar bond(s) (M = Group III or IV metal) with tellurium tetrachloride [10] and also the synthesis of 1-telluracyclopentane 1/1 dipseudohalides and -dicarboxylates [11]. We have now synthesised and characterised a number of tetrahalo-, tetrapseudohalo-, and mixed dihalodipseudohalo-cyclopentanetellurates(IV).

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* For part II see ref. 11.

TABLE I

ANALYTICAL DATA FOR TETRAHALOCYCLOPENTANETELLURATES(IV)

No.	$(R_4M)_2(C_4H_8TeX_2X'_2)$ [a]				M.p. (°C)	Colour	Analysis (Found (calcd.) (%))				
	R	M	X	X′			C	H	N	Te	X [b]
I	Me	N	I	Cl	140(dec.)	Yellow	21.80 (21.94)	5.00 (4.91)	4.25 (4.26)	18.99 (19.42)	50.00 (49.44)
II	Et	N	I	I	153—155	Brick red	25.20 (25.23)	5.00 (5.08)	2.89 (2.94)	13.98 (13.40)	52.80 (53.33)
III	Et	N	I	Br	88—90	Red-brown	27.90 (28.00)	5.58 (5.64)	3.28 (3.26)	14.03 (14.87)	48.58 [c] (48.21)
IV	Et	N	I	Cl	210	Yellow	31.00 (31.24)	5.99 (6.24)	3.72 (3.64)	16.10 (16.59)	41.90 (42.22)
V	Pr	N	I	I	112—113	Orange-pink	31.89 (31.60)	6.00 (6.06)	2.59 (2.63)	11.90 (11.99)	47.00 (47.70)
VI	Bu	N	I	I	98—96	Orange-red	37.01 (36.76)	6.59 (6.85)	2.35 (2.38)	10.00 (10.84)	43.08 (43.15)
VII	Bu	N	I	Br	82—83	Orange-red	40.00 (39.95)	6.99 (7.45)	2.69 (2.58)	11.09 (11.78)	38.69 (38.21)
VIII	Hexyl	N	I	I	64	Orange-pink	43.95 (44.59)	8.00 (8.05)	1.89 (1.94)	8.72 (9.19)	35.80 (36.24)
IX	Heptyl	N	I	I	80—82	Pink	46.38 (47.63)	9.21 (8.52)	1.90 (1.85)	7.79 (8.43)	33.80 (33.55)
X	Ph	P	I	Cl	115—116(dec.)	Yellow	51.99 (52.60)	4.03 (4.07)		9.88 (10.74)	27.39 [c] (27.35)
XI	Ph	P	I	Br	104—107(dec.)	Dark yellow	49.00 (48.90)	3.85 (3.75)		9.74 (9.99)	31.94 [c] (32.41)
XII	Ph	As	I	Cl	130—131(dec.)	Yellow-green	48.75 (48.98)	3.60 (3.79)		10.28 (10.00)	26.00 [c] (25.46)
XIII	Ph	Sb	I	Cl	185(dec.)	Yellow	44.59 (45.63)	3.40 (3.53)		9.80 (9.32)	22.90 (23.72)

[a] Yield 80—100%. [b] Total Halides %. [c] % of I determined, also corresponded to the theoretical value.

Results and discussion

The new complex anions are synthesised through the following reactions:

$$2\ R_4MX + C_4H_8TeI_2 \xrightarrow{\text{Non aq. solv.}} (R_4M)_2[C_4H_8TeI_2X_2] \quad (1)$$

($M = N$; $R = CH_3$, C_2H_5, C_3H_7, C_4H_9, C_6H_{13} or C_7H_{15}; X = Cl, Br or I)
(M = P, As or Sb; $R = C_6H_5$; X = Cl, Br)

$$[C_4H_8TeX_4]^{2-} + 4Y^- \rightarrow [C_4H_8TeY_4]^{2-} + 4X^- \quad (2)$$

(X = Cl, Br or I; Y = I, F, CNO, SCN, N_3)

$$[C_4H_8TeI_2X_2]^{2-} + 2Y^- \rightarrow [C_4H_8TeI_2Y_2]^{2-} + 2X^- \quad (3)$$

(X = Cl or Br; Y = SCN or CNO)

The reactions are essentially quantitative and proceed smoothly under mild conditions. Physical and analytical details of the compounds prepared via reaction 1 are shown in Table 1.

The halogen-exchange reactions represented by eq. 2 provide new complex species not accessible by reaction 1. Thus dichlorodiiodo- and dibromodiiodocyclopentanetellurate(IV) are converted into the tetraiodo derivative (Table 2). The mixed dihalodipseudohalo compounds are prepared by pseudohalide displacement of chloride or bromide rather than iodide from the mixed tetrahalocyclopentanetellurates(IV) (eq. 3 and Table 2).

Molar conductivity values of the complexes are in the range 160—200 Ω^{-1} cm^2 mol^{-1}, 230—290 Ω^{-1} cm^2 mol^{-1} and 52—60 Ω^{-1} cm^2 mol^{-1} (Table 3) in methanol, acetonitrile and nitrobenzene solutions (10^{-3} M) respectively, which shows the compounds to be 2/1 electrolytes [12,13]. The observed molecular weights of the compounds are approximately one third of the formula molecular weight, indicating that the complexes are dissociated into three ions in solution. The calculated value of Van 't Hoff factor ($i \sim 3$) further confirms that the complexes are 2/1 electrolytes.

Infrared spectra

Infrared frequencies due to fundamental modes of vibration of the pseudohalide groups and Te—C bond are listed in Table 2. Vibrational frequencies associated with cations are similar to those reported [14] and are not tabulated. Absorptions associated with the various modes of vibration of the pseudohalide groups have been identified and indicate the nature of their bonding to tellurium metal. The chalcogenate group NCX (X = S or O) gives rise to three fundamental modes of vibration due to ν(C≡N), ν(C—X) and δ(NCX). The observed frequencies for these modes of vibration are listed in Table 2 and are consistent with the iso structure of the compounds containing Te—N bonding [15]. Characteristic absorptions of N_3 stretchings and bending modes show the presence of covalently bonded linear N=N=N group [11,16]. Absorption associated with Te—C bond is observed as a strong band in the region 520—560 cm^{-1} for 1-telluracyclopentane derivatives which is slightly hugher than the Te—C frequency in dimethyl- (472—544 cm^{-1}) [17] and diethyl-tellurium dihalides (460—560 cm^{-1}) [18] which may be attributed to steric effects [19].

TABLE 2

ANIONIC COMPLEXES OBTAINED BY HALOGEN EXCHANGE REACTIONS WITH (Y^-)

	Reactants		Product [b] $(R_4M)_2(C_4H_8TeX_2Y_2)$				M.p. (°C)	Colour
	Compd. no. [a]	Y^-	R	M	X	Y		
XIV	XI	I^-	C_6H_5	P	I	I	200(dec.)	Orange-brown
XV	XII	I^-	C_6H_5	As	I	I	210	Red-purple
XVI	XII	NCS^-	C_6H_5	As	I	NCS	147—148(dec.)	Yellow
XVII	X	NCO^-	C_6H_5	P	I	NCO	172(dec.)	Yellow
XVIII	II	NCO^-	C_6H_5	N	CNO	NCO	164	White
XIX	VII	N_3^-	C_7H_{15}	N	N_3	N_3	162	White
XX	VIII	F^-	C_6H_{13}	N	F	F	235	White

[a] See Table 1. [b] Yield 90—100%. [c] % of total (I + SCN) 28.00 (28.02). [d] Abbreviations: v, very; s, strong; m, med w, weak.

TABLE 3

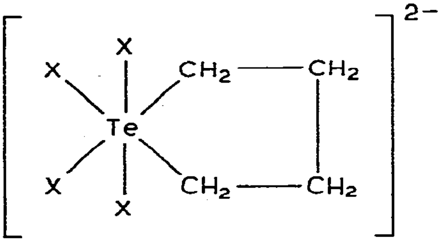
MOLAR CONDUCTANCES (10^{-3} *M* solution) AND VAN 'T HOFF FACTORS (*i*) FOR REPRESENTATIVE ANIONIC COMPLEXES

Compd. no. [a]	Molar conductance (Ω^{-1} cm^2 mol^{-1})			Van 't Hoff factor (*i*)
	CH_3CN	CH_3OH	$C_6H_5NO_2$	
II	230.2	160.2	55.9	2.97
III	232.0	160.8	56.2	3.05
V	230.4	165.2	56.3	3.00
VII	245.8	168.1	58.8	2.84
IX	246.7	164.1	57.2	2.99
X	248.8	165.4	59.0	2.96
XII	255.9	170.5	59.8	3.07
XIII	272.2	188.5	60.2	3.03
XIV	280.1	190.6	60.9	3.00
XV	275.0	180.8	59.2	2.99
XVI	238.2	170.9	56.4	3.01
XVII	245.3	180.0	58.2	2.99
XVIII	240.4	164.0	55.8	3.00
XIX	245.5	170.1	57.9	3.02

[a] See Tables 1 and 2.

Analysis (Found (calcd.) (%))					Absorption frequencies (cm^{-1}) ^{d}			
C	H	N	Te	X	ν_{asym} pseud.	ν_{sym} pseud.	δpseud.	ν(Te—C)
45.50 (45.58)	3.60 (3.53)		8.98 (9.31)	36.50 (37.04)				530s
			9.00 (8.75)	35.19 (34.81)				550s
			9.00 (9.66)	19.50 ^{c} (19.22)	2045vs	350m	472m	550s
			10.89 (10.63)	22.02 (21.14)	2180vs	1300m	615m	520s
47.50 (47.08)	7.98 (7.90)	13.80 (13.72)	20.99 (20.83)		2180vs	1285m	614m	540s
61.00 (61.41)	11.02 (10.99)	16.00 (16.71)	11.00 (10.89)		2105vs	2105m	672w	550s
64.40 (64.45)	11.58 (11.64)		13.84 (13.16)					

Tetrahalotelluracyclopentane anions are tentatively assigned an octahedral structure, with the cyclopentane group occupying the *cis* position.



NMR spectra

The NMR spectra of $[(C_3H_7)_4N]_2[C_4H_8TeI_4]$ and $[(C_6H_5)_4As]_2[C_4H_8TeI_2Cl_2]$ were recorded at room temperature. A multiplet in the region τ 2—2.9 is due to phenyl ring protons. Two multiplets are observed in the region τ 6.72—7.45 in telluracyclopentane derivatives. The multiplet at τ 6.07—6.50 may be attributed to $—CH_2—Te$ (2,5) protons, whereas the multiplet at τ 6.90—7.30 corresponds to $—CH_2—C$ (3,4) protons [20]. A triplet at τ 8.90 and two multiplets at τ 6.65 and τ 8.23 may be assigned to $—CH_3$, $—CH_2—N$, and $—C—CH_2—C$ protons in the spectra of $[(C_3H_7)_4N]_2[C_4H_8TeI_4]$. The spectra, including the integrations, correspond to the proposed stoichiometry of the compounds.

Experimental

1-Telluracyclopentane 1/1 diiodide [21], tetraphenylphosphonium bromide, tetraphenylarsonium chloride and tetraphenylstibonium chloride [22] were prepared by reported methods. Tetraalkylammonium halides of B.D.H. grade were used. Molecular weight was determined cryoscopically using Beckmann thermometer of accuracy of ±0.01° C. The molar conductance of 10^{-3} M solutions was determined at 25° C with a Philips conductivity assembly PR-9500. Infrared spectra were recorded in KBr or Nujol in the region 4000—400 cm^{-1} with Perkin—Elmer model Infrared Cord spectrometer 337. Proton magnetic resonance spectra were recorded at room temperature in $CDCl_3$ with a Varian A60 D or A90 D spectrometer, using tetramethylsilane as internal standard.

Preparation of anionic complexes

(i) Tetraorganoammonium, -phosphonium, -arsonium, -stiboniumtetrahalocyclopentanetellurates(IV). The complexes were made according to eq. 1 and are listed in Table 1. 1-Telluracyclopentane 1/1-diiodide (1 mmol) was refluxed with a solution of tetraorgano-ammonium, -phosphonium, -arsonium, or -stibonium halides (2 mmol) in chloroform or ethanol for 4—5 h. The solution was concentrated and the complex precipitated by addition of excess of petroleum ether (60—80° C). It was recrystallized from acetone/petroleum ether (60—80° C) and dried in vacuum.

(ii) Halogen exchange reaction: conversion of tetrahalotellurates into tetraiodotellurates. An aqueous solution of potassium iodide (in excess) was added to a solution of bis(tetraphenylarsonium)dichlorodiiodocyclopentanetellurate(IV) (1 mmol) in 4 N HCl with constant stirring (eq. 2). The corresponding tetraiodo compound was precipitated in quantitative yield, filtered, washed with water and dried, m.p. 210° C.

(iii) Pseudohalogen exchange reaction: conversion of tetrahalotellurates into tetra-cyanato, -azido or -thiocyanatotellurates(IV). In a typical reaction bis(tetraethylammonium)tetraiodocyclopentanetellurate(IV) (1 mmol) was stirred with silver or potassium cyanate (4 mmol) (eq. 2) in chloroform for 2 h and then refluxed for additional 3—4 h. The precipitated potassium or silver salt was removed, and the filtrate on concentration gave the corresponding bis(tetraethylammonium)tetracyanatocyclopentanetellurate(IV). Yield 99%, m.p. 164° C.

(iv) Conversion of diiododichloro- or diiododibromo-tellurates into diiododipseudohalotellurates. In a typical reaction bis(tetraphenylarsonium)diiododichlorocyclopentanetellurate(IV) (1 mmol) was stirred with silver or potassium thiocyanate (2 mmol) in chloroform (eq. 3) for 2 h and then refluxed for 3—4 h. The precipitated silver or potassium salt was filtered off, and the solution evaporated to yield the corresponding diiododiisothiocyanatotellurate(IV) in 98% yield, m.p. 147—148° C (dec.).

(v) Preparation of bis(tetrahexylammonium)tetrafluorocyclopentanetellurate. Bis(tetrahexylammonium)tetraiodocyclopentanetellurate(IV) (1.39 g, 1 mmol) was crushed with freshly prepared silver oxide (0.464 g, 2 mmol) in minimum quantity of water and filtered. The filtrate was collected in a platinum crucible and neutralised with hydrofluoric acid. The solution was evaporated under reduced pressure over sulfuric acid, and the resulting solid recrystallized from acetone.

Acknowledgement

The authors thank the Head of Chemistry Department, Lucknow University for providing necessary laboratory facilities and M.S. is grateful to the Council of Scientific and Industrial Research, New Delhi for an award of a J.R.F.

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