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SYNTHESIS AND CONFIGURATIONS OF 2-METHYL-1-ORGANO-1-HALO-1-TELLURACYCLOPENTANES

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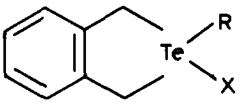
Summary

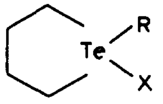
Some new cyclic telluronium salts ($C_5H_{10}TeRX$: $R = CH_3$, CH_2CH_3, $X = I$; $R = CH_2Ph$, $X = Br$) have been prepared by oxidative addition of alkyl halides to 2-methyl-1-telluracyclopentane. The *cis/trans* ratio in the product mixture was determined by ^1H NMR spectroscopy.

Introduction

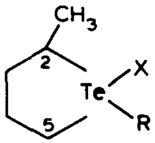
Recent studies [1–3] on the synthesis and spectra of the tellurium compounds I and II prompted the preparation of a series of telluronium salts derived from



(I) [1]



(II) [2,3]



(III)

	R	X
IIIa	I	I
IIIb	CH_3	I
IIIc	CH_2CH_3	I
IIId	CH_2Ph	Br

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2-methyl-1-telluracyclopentane (III).

An X-ray study [4] on compounds of type I showed the presence of a planar ring with Te–alkyl group *trans* to a halide in distorted octahedral coordinate geometry. This geometry arose from a weak associative interaction. This suggested to us that it might be possible with telluronium salts of type III to delict the presence of *cis* and *trans* isomers.

Experimental

This was prepared by a slight modification of the method described earlier [1,2,5,6].

2-Methyl-1,1-diiodo-1-telluracyclopentane (IIIa)

A mixture of 1,4-dibromopentane (6.90 g, 0.03 mol), tellurium powder (2.55 g, 0.02 g-atom), sodium iodide (9.0 g, 0.06 mol) and 2-butoxyethanol (100 ml) was heated gently with stirring for 2 h. Gentle boiling then gave a heavy orange precipitate. Addition of 200 ml of water to the cold solution caused further precipitation. The product was filtered off, washed with water, then acetone, and air dried. Recrystallisation from DMF yielded orange crystals, m.p. 110–112°C. Found: C, 13.3; H, 2.23. $C_5H_{10}TeI_2$ calcd.: C, 13.3; H, 2.40%.

1,2-Dimethyl-1-iodo-1-telluracyclopentane (IIIb)

Sodium borohydride was added to a boiling methanolic solution of 2-methyl-1,1-diiodo-1-telluracyclopentane (IIIa) until the orange colour disappeared. The solution was filtered, then added to 1 l of water. After extraction with ether the extract was washed with water, dried over $CaCl_2$, and concentrated on a rotary evaporator. An excess of freshly distilled iodomethane was then added and the vessel was stoppered and set aside overnight. The white solid obtained was washed with ether and dried over P_4O_{10}. White crystals were obtained by recrystallization from a mixture of ethanol and water (3/1). m.p. 215°C (dec.). Found: C, 21.2; H, 3.30. $C_6H_{13}TeI$ calcd.: C, 21.3; H, 3.28%.

The following compounds were prepared by similar reaction of appropriate alkyl halide with 2-methyl-1-telluracyclopentane.

1-Ethyl-2-methyl-1-iodo-1-telluracyclopentane (IIIc). White crystals after recrystallisation from ethanol/water (3/1), m.p. 165–167°C (dec.). Found: C, 23.6; H, 4.40. $C_7H_{15}TeI$ calcd.: C, 23.8; H, 4.28%.

2-Methyl-1-benzyl-1-bromo-1-telluracyclopentane (IIId). White crystals after recrystallization from a mixture of ethanol and water (3/1), m.p. 168°C (dec.). Found: C, 37.7; H, 4.30. $C_{12}H_{17}TeBr$ calcd.: C, 37.4; H, 4.28%.

Physical measurements

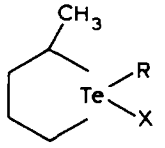
^1H NMR spectra were measured in DMSO-d_6 on a Bruker WH 90C spectrometer. The data are listed in Table 1.

Discussion

Three new telluronium salts which, to our knowledge, are the first example of substituted telluracycles were obtained from reactions of 2-methyl-1-telluracyclopentane with the appropriate alkyl halides. The synthesis of the new diiodide (IIIa) using a boiling solvent and excess of sodium iodide avoids the use of a sealed-tube reaction such as was previously used for a number of dialkyltellurium diiodides [7].

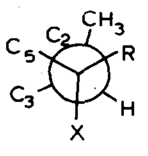
The ^{1}H NMR spectra (90 MHz; relative to TMS) of compounds IIIb and IIIc show the presence of a mixture of *cis/trans* geometrical isomers (IV and V), Fig. 1 and Table 1, with the *trans*-isomer predominating. The isomer ratio was found to be greatly affected by the size of the alkyl group attached to tellurium atom (see Table 2). This can be understood in terms of the *gauche* and *anti* conformations shown below as Newman projections along Te–C_2 bond (Compare the situation for butane [8]).

Peak assignments were based on intensity, multiplicity, and structure, taking account of the downfield chemical shift for the *trans* form, [9]. Thus for $R = CH_3$ (compound IIIb), the spectrum showed four signals for the C_2–Me and Te–Me protons; the first (low intensity, highfield) doublet (J 7 Hz) at δ 1.45 ppm, was assigned to *cis* C_2–Me and the next doublet downfield (of high intensity) (J 7 Hz) at δ 1.60 ppm to *trans* C_2–Me. The two downfield singlets at δ 2.10 and 2.20 ppm were assigned to the *cis* and *trans* Te–Me resonances, respectively. Integration of these signals gave a *cis/trans* ratio of 39/61 (Table 2). Replacement of the methyl by an ethyl group caused a marked shift in favour of the *trans* isomer. Unfortunately the complexity of the spectrum due to the overlap of *cis* C_2–Me with the ethyl group makes it difficult to give an accurate value for the ratio, but it is ca. 27/73. Replacement of the methyl group by a benzyl group (Fig. 1) led to the appearance of only one doublet, at δ 1.70 ppm, with a chemical shift appropriate for *trans* C_2–Me, along with a sharp singlet at δ 4.30 ppm due the benzyl methylene protons, thus only the *trans*-isomer is present.

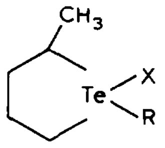


(IV)
cis

$|||$

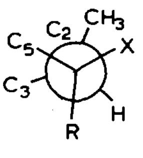


gauche



(V)
trans

$|||$



anti

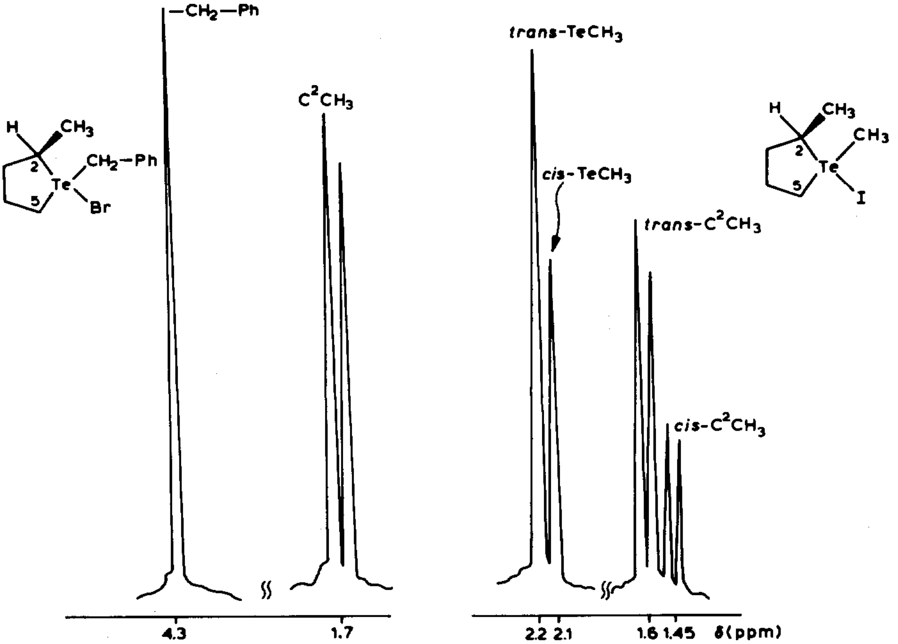


Fig. 1. ^1H NMR spectra for compounds IIIb and IIId in DMSO.

TABLE 1

^1H NMR DATA FOR 2-METHYL-1-TELLURACYCLOPENTANES (90 MHz, DMSO) rel. to TMS) 0 ppm

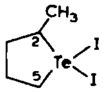
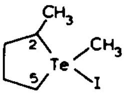
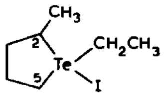
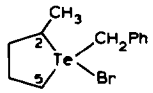
Compound	Chemical shift δ (ppm)	Assignment	
	1.90	doublet (J 7 Hz)	C_2CH_3
	2.20–2.55	complex multiplet	3-H
	2.85–3.2	complex multiplet	4-H
	4.45–3.80	complex multiplet	2-H
	3.80–4.25	complex multiplet	5-H
	1.45	doublet (J 7 Hz)	C_2CH_3 *cis*
	1.60	doublet (J 7 Hz)	C_2CH_3 *trans*
	2.10	singlet	$TeCH_3$ *cis*
	2.20	singlet	$TeCH_3$ *trans*
	1.80–2.75	complex multiplet	3,4-H
	2.95–3.15	complex multiplet	5-H
	3.60–3.90	complex multiplet	2-H
	1.55–1.75	complex multiplet	*cis* $C_2Me-CH_2CH_3$
	1.95	doublet (J 7 Hz)	C_2Me *trans*
	2.35–2.65	complex multiplet	3,4-H
	3.25	quartet (J 7 Hz)	CH_2CH_3
	1.70	doublet (J 7 Hz)	C_2Me *trans*
	1.70–2.35	complex multiplet	3,4-H
	2.88–3.65	complex multiplet	2,5-H
	4.30	s	Benzyl-CH_2
	7.45	s	Ar-H

TABLE 2

cis/trans RATIO IN 2-METHYL-1-TELLURACYCLOPENTANE DERIVATIVES

Compound	*cis/trans* ratio
IIIb	39/61
IIIc	ca. 27/73
IIId	0/100
IIIa	0/100

Studies of the solid state and solution properties of this type of telluronium salt are in progress.

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