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A New Range of Heterocyclic Telluronium Salts Based on 1,2,4,5-Bis(telluracyclopentano)benzene: Synthesis and Spectroscopic Considerations

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ABSTRACT

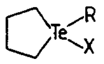
The reactions of 1,2,4,5-tetrakis(bromomethyl)-benzene with sodium organotellurates (NaTeR) afford white telluronium salts of the type $XRTe(CH_2)_2C_6H_2(CH_2)_2TeRX$ *where* $R = p\text{-}EtOC_6H_4$ *and* $p\text{-}MeOC_6H_4$ *and* $X = Br$.

Reactions of 1,2,4,5-tetrakis(bromomethyl)-benzene with elemental tellurium powder and an excess of sodium iodide in dimethyl sulfoxide (DMSO) give 1,2,4,5-bis(1,1-diiodotelluracyclopentano)benzene, $C_{10}H_{10}Te_2I_4$ *as orange-red crystals in poor yield, together with a yellow amorphous precipitate as the main product, the structure of which is still obscure.*

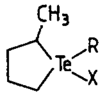
Reduction of the bis(diiodide) compound gave a light and air sensitive ditelluride, $C_{10}H_{10}Te_2$*, which, on treatment with ethyl bromide, afforded a white telluronium salt of 1,2,4,5-bis(1'-bromo-1'-ethyl-telluracyclopentano)benzene,* $C_{14}H_{20}Te_2Br_2$*. The synthesis, spectroscopic data, and solution properties of the prepared compounds are reported and discussed.*

INTRODUCTION

Several articles on the synthesis and spectra of heterocyclic telluronium salts derived from the telluracyclopentane unit have appeared in the literature [1–3]. The salts were commonly prepared by the oxidative addition of an alkyl halide to the desired telluride (compounds I–III). Furthermore, McWhinnie and co-workers [4] reported the successful cyclization and salt formation, particularly for five-membered ring telluronium salts, by the action of a sodium organotellurate on an open chain 1,4-dihaloalkane to give compounds of type IV.



I



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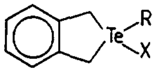

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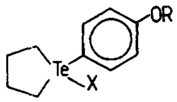

IV

Therefore, the preparation of numerous other telluronium salts having bis(telluracyclopentane) units appears feasible. In this article, new heterocyclic telluronium salts (series V) have been prepared and characterized. Singh et al. [5] recently claimed the preparation of the bis(diiodide), compound Vd, as a yellow precipitate and in 80% yield. The present research shows that this report is incorrect.

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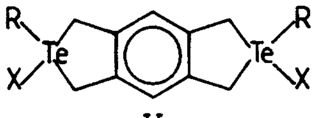


V

Comp.	R	X
Va	$MeOC_6H_4$	Br
Vb	$EtOC_6H_4$	Br
Vc	Et	Br
Vd	I	I

EXPERIMENTAL

Synthesis

Di(*p*-methoxyphenyl) and di(*p*-ethoxyphenyl) ditellurides $(RTe)_2$, which are used in this investigation, were prepared by the literature method [6]. Compounds Va and Vb were prepared by adopting a previous method [4]. The reaction of di(*p*-ethoxyphenyl) ditelluride with 1,2,4,5-tetrakis-(bromomethyl)benzene in the presence of ($NaBH_4$/NaOH) is illustrated.

1,2,4,5-Bis[(1'-bromo-1'-p-ethoxyphenyl)-telluracyclopentano]benzene, Vb

Sodium borohydride (22 mmol) in 20 mL of 1 M aqueous or ethanolic sodium hydroxide solution was added dropwise to a refluxing solution of di(*p*-ethoxyphenyl) ditelluride (14 mmol) in (12:20 mL) of a benzene/ethanol mixture under nitrogen. When the starting yellow-red solution became colorless, 1,2,4,5-tetrakis(bromomethyl)benzene (1 mmol) was added and the warm mixture was stirred for 1 hour. A white precipitate was filtered off, washed with ether, and dried in vacuo. Recrystallization from ethanol/water gave an analytically pure white precipitate.

1,2,4,5-Bis[(1'-bromo-1'-*p*-methoxyphenyl)telluracyclopentano]benzene, compound Va, was prepared similarly. The data on elemental analyses and physical properties are given in Table 1.

1,2,4,5-Bis(1',1'-diiodotelluracyclopentano)-benzene, Vd

A mixture of 1,2,4,5-tetrakis(bromomethyl)-benzene (0.01 mol), tellurium powder (0.02 mol), and sodium iodide (0.08 mol) in 100 mL of dimethyl sulfoxide was stirred at 98–100°C for 3 hours. After cooling the mixture, deionized water (200 mL) was added. A yellow-orange precipitate was obtained, filtered off, and dried. Recrystallization from dimethylformamide (DMF) gave orange-red crystals (initially precipitated) identified as Vd (10–14% yield). Later, a yellow amorphous precipitate started to deposit (almost 80–90% of the total solid mass).

Note. The above reaction has been carried out over the range of temperatures 80–160°C and in various solvents, including 2-methoxyethanol which was used for the preparation of Vd by Singh et al. [5]. In each case, only a yellow amorphous precipitate or (in some cases) a deep yellow precipitate was isolated. The yellow amorphous product has mp 226–228°C and its elemental analysis is as follows. Found: C, 18.49; H, 1.82; and I, 62.49%. ^1H NMR, δ (DMSO-d_6), 4.4–4.8 (broad singlet, 8H); 7.6 (S, 2H, Ar-H). The deep yellow precipitate has mp > 300°C and elemental analysis as follows. Found: C, 9.39; H, 0.88%.

1,2,4,5-Bis[(1'-bromo-1'-ethyl)telluracyclopentano]benzene, Vc

Sodium borohydride was added slowly to a boiling methanolic solution of the 1,1-bis(diiodide), Vd, until the orange color disappeared. The solution was filtered, and the filtrate was added to 500 mL of deionized water and extracted with ether. The yellow ether extract was shaken with $MgSO_4$, filtered, flashed with nitrogen, and rapidly treated with an excess of freshly distilled ethyl bromide. The vessel was stoppered and set aside overnight in a dark place. A precipitated white solid was filtered off, washed with ether, and dried. Recrystallization from ethanol gave a white precipitate in a very low yield. Yield and physical properties are given in Table 1.

Physical Measurement

The ^1H and some ^{13}C NMR spectra were recorded on Bruker WM 250 AC and MH_z Ex-90 JEOL FT-NMR spectrometers. Analytical measurements were carried out by the Analytical Service Unit, Fakulat fur Chemie, Universitat Konstanz, Federal Republic of Germany. The IR spectra were recorded on a Pye-Unicam 2000 spectrometer with (KBr disk) in a range of 200–4000 cm^{-1}. Mass spectra were obtained at 70 ev with an AEI-MS9 instrument. Solution conductivities were measured with a WTW conductivity meter LBR, using a standard conductivity cell with a cell constant of 0.0577.

RESULTS AND DISCUSSION

The prepared compounds were characterized on the basis of their elemental analyses and ^1H and ^{13}C NMR and IR spectra. Data are presented in Tables 1–3. The new heterocyclic telluronium salts, com-

TABLE 1 Analytical and Physical Properties of Compounds Va–Vd

Compound	*Yield %*	*Color and Solid State*	*mp (°C)*	*H %*	*C %*	*Te %*[a]
Va	66	white ppt	254–2 (dec)	2.77 (3.18)[b]	37.44 (37.96)[b]	—
Vb	68	white ppt	246–2	3.32 (3.58)	38.96 (39.66)	31.98 (32.31)
Vc	2–4	white ppt	148–2 (dec)	3.04 (3.30)	27.55 (27.91)	—
Vd	10–14	orange-red crystal	248–2	1.15 (1.13)	13.70 (13.44)	28.46 (28.44)

[a] Following the method of Thavornyutikarn [7].

[b] Figures in parentheses are theoretical values.

TABLE 2 ^1H and ^{13}C NMR Data for Compounds Va–Vd in DMSO-d_6

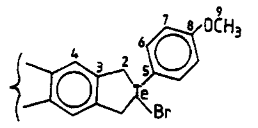
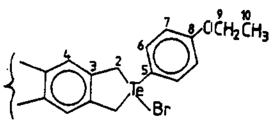
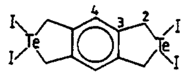
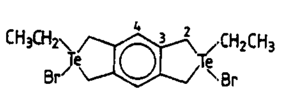
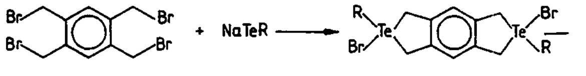
Compounds	*^1H*	*^{13}C*
	OCH_3, 3.96 (s, 6H); ring CH_2, 4.02–4.96 (q, J = 15 Hz, 8H); 7.8–8.2 (m, 10H, aromatic)	33.98 (C^2), 138.44 (C^3), 122.28 (C^4), ? (C^5), 136.44 (C^6), 114.92 (C^7), 159.66 (C^8), 63.88 (C^9)
	OCH_2, 4.4 (q, 4H); CH_3, 1.82 (t, 6H); ring CH_2, 3.98–4.20 (q, J = 15 Hz, 8H); 7.2–7.8 (m, 10H, aromatic)	34.66 (C^2), 139.37 (C^3), 122.66 (C^4), ? (C^5), 136.80 (C^6), 115.82 (C^7), 160.11 (C^8), 63.76 (C^9), 14.49 (C^{10})
	CH_2, 4.76 (s, 8H); 7.40 (s, 2H, aromatic)	—
	CH_3, 1.28 (t, 6H); CH_2, 2.26 (q, 4H), ring CH_2, 4.04–4.36 (q, J = 15 Hz, 8H); 7.20 (s, 2H, aromatic)	—

TABLE 3 IR and Conductivity Data (10^{-3} M) for Compounds Va–Vd

	Molar Conductance Λm 10^{-3} M ohm^{-1} · cm^2 · mol^{-1}		*ν cm^{-1}*	
	Solvent			
Compound	*DMSO*	*DMF*	*ν(Te–C Ring)*	*ν(Te–C Alkyl)*
Va	24	48	470w	265w[a]
Vb	22	44	465w	260w[a]
Vc	46	106	500w	535m
Vd	56	119	505w	—

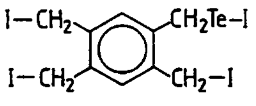
[a] For ν(Te–C phenyl).

pounds Va and Vb, are conveniently prepared by the reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with the freshly generated sodium (*p*-alkoxyphenyl)tellurate solution under nitrogen (Equation 1) in a good yield (Table 1). The reaction mechanism seems to be similar to those observed previously [4], namely, a nucleophilic attack by the generated organotellurium anion (RTe^-) followed by a rapid quarternization.

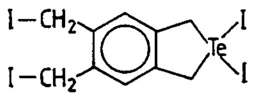


(1)

Several attempts were made to investigate the possibility of formation of the bis(diiodide), compound Vd, by the reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with NaI and tellurium powder in various solvents (except DMSO) and under the same conditions as used for other tellurium diiodide preparations [1,2,8]. However, all such efforts met with failure and only a yellow amorphous precipitate (or, in some cases, a deep yellow precipitate) was isolated. The yellow amorphous product has limited solubility in $CHCl_3$ and DMSO, and when it was reduced with $NaBH_4$ in hot ethanol, a greenish solution was obtained which changed to gray and then to black because of a free tellurium deposit. Its ^1H NMR spectrum in DMSO-d_6 is similar but not identical to that observed for the bis(diiodide) Vd, particularly for the resonance of methylene protons. The spectrum showed a broad singlet of an unresolved multiplet at δ 4.4–4.8 (see the Experimental section). The ^1H NMR spectrum and elemental analysis data of 62.49% of iodine content, for the yellow amorphous precipitate, suggest that this product is presumably like one of the suggested formulations, VIa or VIb (calcd: C, 15.68; H, 1.31: I, 66.40%).



VIa

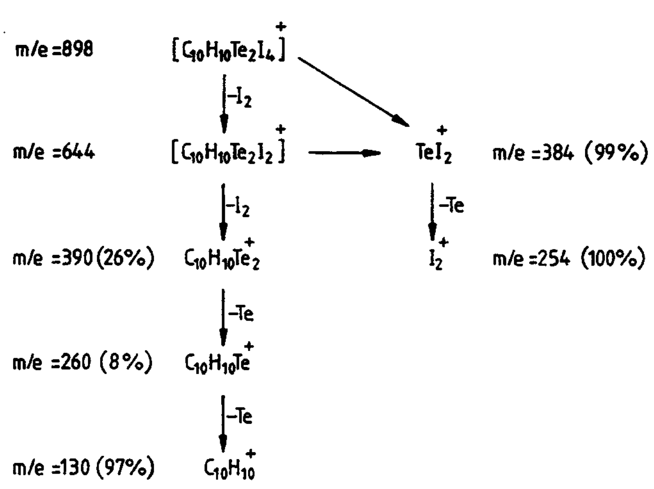


VIb

The deep yellow precipitate was almost insoluble in most organic solvents, and when it was submitted to similar reduction, a pink-violet solution was obtained which quickly changed to white and then to a black solution having a free tellurium deposit. Its constitution remained obscure.

When 1,2,4,5-tetrakis(bromomethyl)benzene was allowed to react similarly in DMSO solution under the conditions cited (see the Experimental section), the bis(diiodide), Vd, was isolated as orange-red crystals. The reaction was repeated over a range of temperatures, and the yield fluctuated irregularly with conditions from 4–6%. The only modestly satisfactory result was obtained by heating the mixture at 98–100°C for 3 hours. Repeated experiments gave a 10–14% yield of Vd.

In addition to the correct elemental analysis and ^1H NMR spectrum of the bis(diiodide), Vd (Tables 1 and 2), the mass spectrum of Vd showed fragments consistent with structure Vd. The following major fragments were observed: m/e = 390($C_{10}H_{10}Te_2^+$, 26%), 260($C_{10}H_{10}Te^+$, 8%), 130($C_{10}H_{10}^+$, 97%), 384(TeI_2^+, 99%), and 254(I_2^+, 100%). The fragmentation involved successive losses of iodine and tellurium leading to the cycloalkane cation formation. This observation is in good agreement with previous investigations for other diiodides [8,9]. A suggested pathway is presented in Scheme 1.



SCHEME 1

When the bis(diiodide), Vd, was reduced with $NaBH_4$ in hot ethanol, it afforded the corresponding ditelluride,1,1-bis(telluracyclopentano)benzene. Unfortunately, the product was found to be sensitive to both light and air. Therefore, it rapidly reacted with ethyl bromide (see the Experimental section) to give the new telluronium salt of 1,2,4,5-bis[(1′-bromo-1′-ethyl)telluracyclopentano]benzene, compound Vc. These observations are in disagreement with those claimed by Singh et al. [5] for the synthesis of the bis(diiodide), compound Vd. Their results are inconsistent with the proposed structure. The reported carbon content (C, 15.1%) in combustion analysis did not correspond to the formula $C_{10}H_{10}Te_2I_4$ (calcd: C, 13.44%). In addition, the mass spectral scheme presented by Singh et al. is questionable. Moreover, the proposed fragmentation of the latter ion, which is an even electron species, to give the odd electron ion HI (m/e = 128 amu) is clearly in contradiction with the well-known even-electron rule [10].

The ^1H NMR spectra of compounds Va and Vb (Table 2) showed the correct ratio of aromatic to aliphatic protons, supporting the stoichiometry and purity of the material. However, the formation of telluronium salts Va–Vc showed a remarkable change in the methylene ring protons which appeared as a quartet of an AB pattern, with a $^2J(HH)$ value of almost 15 Hz.

The ^{13}C NMR spectra of compounds Va and Vb were obtained in DMSO-d_6 (Table 2) which provided good support for the proposed structures. The observed chemical shift of δ 33–34 for the ring methylene carbon is in good agreement with detailed published data [1,3,4].

The conductivity data in both solvents DMSO and DMF are summarized in Table 3. Compounds Va and Vb showed low molar conductance Λm values which, in general, are similar to those observed for structurally related compounds IV [4] are probably due to considerable ion-pairing. For compounds Vc and Vd, the *Am* values in DMSO and DMF fall in the range of 46–56 and 106–119 ohm · cm^2 · mol^{-1} (Table 3). The values almost approach those expected for a (1:2) electrolyte [11,12]. Also, in contrast, the *Am* value of (119 ohm^{-1} · cm^2 · mol^{-1}) for the bis(diiodide) in DMF is nearly double that found previously for 1,1-diiodo-3,4-benzo(telluracyclopentane) 70 ohm · cm^2 · mol^{-1} [8].

The IR spectra of compounds Va–Vd (KBr disc) gave little structural information. Data are listed in Table 3. We tentatively assign the bands between 465–505 cm^{-1} to ν(Te-C ring), and those between 260–535 cm^{-1} to ν(Te-C alkyl) by considering previous works [1,3,13].

ACKNOWLEDGMENT

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