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# ORGANOTELLURIUM DERIVATIVES OF DICARBOXYLIC ACIDS

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## Summary

The freshly prepared sodium salts of *ortho*-phthalic acid and tetrabromo *ortho*-phthalic acid react with diaryltellurium dichlorides in chloroform to afi new dimeric organotellurium carboxylates, $R_2Te(C_8X_4O_4)_2$ (X = H, Br). The new compounds contain fourteen membered rings and the detailed structure is discussed particularly in the light of the $^1$H NMR spectrum of $(p\text{-}EtOC_6H_4)_2Te(C_8H_4O_4)_2$ which shows inequivalence of *p*-ethoxy groups.

The sebacate derivatives of tellurium(IV) are oligomeric and iso- and tere phthalic acids failed to give well defined products.

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## Introduction

Recent papers have reported, in one instance, new preparative routes to organotellurium dicarboxylates [1] and, in another, their vibrational spectra [ We have been interested in the synthesis of compounds of the type $R_2Te^{IV}$-(chelate) where R is an aryl group and chelate represents a di-negative anionic group which could be a dicarboxylate group. We wished to ascertain the molecular complexity of such compounds and to investigate, should monomers be formed, the differences in the "axial" and "equatorial" Te—C bonds where tl descriptions assume that the structure may be regarded as $\psi$-trigonal bipyram al with an axial position occupied by a non-bonding pair of electrons. In practice interesting dimers were obtained with *o*-phthalates and oligomers with sebacic acid; *p*- and *m*-phthalates gave ill defined products. These materials ar briefly discussed below.

## Experimental

Infrared spectra were obtained for nujol mulls with a Perkin—Elmer 237 instrument and for chloroform solutions with a Perkin—Elmer 457 instrument. Molecular weights were determined by vapour phase osmometry, using benzene as solvent, with a Knauer vapour pressure osmometer. $^1$H NMR spectra were taken at 100 MHz for $CDCl_3$ solutions (where solubility permitted) with a Varian R10 instrument (TMS internal standard).

### *Preparations*

*With o-phthalic acid.* Initial attempts to react diphenyltellurium dichloride or dibromide at their melting points with *o*-phthalic acid afforded only phthalic anhydride. A successful method was developed based on the sodium salt of the acid: phthalic acid (2.5 g, 0.05 *M*) in water (100 ml) is treated with aqueous sodium hydroxide until almost neutral. The solution is evaporated to dryness and the residue is finely ground and treated with a chloroform (50 ml) solution of $R_2TeCl_2$ (0.012 mol) (R = Ph, *p*-$MeOC_6H_4$ or *p*-$EtOC_6H_4$). The reaction mixture is shaken for 48 h at room temperature and then filtered to remove sodium chloride and unreacted sodium phthalate. The organotellurium carboxylate is recovered from the filtrate and recrystallised from petroleum ether/benzene in 50-85% yield. (N.B. Use of $R_2TeBr_2$ gives only a very slow reaction with poor yields). A similar method may be used to prepare diphenyltellurium tetrabromophthalate and di(*p*-methoxyphenyl)tellurium *o*-tetrabromophthalate. Diphenyltellurium *o*-phthalate (n.c.) m.p. 108-110°C. (Found: C, 52.0; H, 3.29. $C_{20}H_{14}O_4Te$ calcd.: C, 53.9; H, 3.15%.) Di(*p*-methoxyphenyl)tellurium *o*-phthalate (n.c.) m.p. 90-95°C (dec.). (Found: C, 49.8; H, 3.60. $C_{22}H_{18}O_6Te$ calcd.: C, 52.2; H, 3.56%.) Di(*p*-ethoxyphenyl)tellurium *o*-phthalate (n.c.) m.p. 129-131°C. (Found: C, 52.1; H, 4.0. $C_{24}H_{22}O_6Te$ calcd.: C, 54.0; H, 4.13%.) Diphenyltellurium *o*-tetrabromophthalate (n.c.) m.p. 92-93°C. (Found: C, 32.3; H, 2.18. $C_{20}H_{10}Br_4O_4Te$ calcd.: C, 31.6; H, 1.31%.) Di(*p*-methoxyphenyl)tellurium *o*-tetrabromophthalate (n.c.) m.p. 98-102°C (dec.). (Found: C, 32.6; H, 2.20; Br, 42.0. $C_{22}H_{14}Br_4O_4Te$ calcd.: C, 32.0; H, 1.69; Br, 42.5%.)

Molecular weight determinations were carried out where solubility in benzene permitted with the results shown in Table 1.

The extension of the above method to other acids was less successful. Thus no pure products were obtained with maleic, fumaric or formic acid. Also iso- and terephthalic acids failed to give isolable pure compounds. We also attempted to use a method reported by Prasad [3] to produce a tellurium(IV) tetra-

TABLE 1

MOLECULAR WEIGHTS

| | M(monomer) | M(dimer) | M(obs.) |
|---|---|---|---|
| $Ph_2Te(C_8H_4O_4)$ | 445 | 890 | 880 |
| $(MeOC_6H_4)_2Te(C_8H_4O_4)$ | 505 | 1010 | 940 |
| $Ph_2Te(C_8Br_4O_4)$ | 762 | 1524 | >1000 |

carboxylate but in our hands the reaction of $TeCl_4$ with RCOOH failed to afford $Te(OOCR)_4$. A modification using the sodium salt of the acid was also unsuccessful.

We finally attempted to react the sodium salt of sebacic acid with diphenyltellurium dichloride and with di(*p*-methoxyphenyl)tellurium dichloride and obtained in each case glass like material which gave a molecular weight corresponding approximately to trimers. This result contrasts an earlier report [4] in which oligomers of rather larger average molecular weight were obtained.

## Discussion

### *Diorganotellurium o-phthalates*

It proved possible to synthesise organotellurium esters of *o*-phthalic acid via the freshly prepared sodium salts. However the method did not appear to be generally applicable to the preparation of similar derivatives of other dicarboxylic acids. It was also apparent that a satisfactory preparative route was possible only if a diaryltellurium dichloride was used.

Some compounds were sufficiently soluble in benzene for molecular weights to be obtained and the results rather clearly indicate that the compounds must be formulated as dimers. Thus an interesting monomeric structure involving "long" and "short" tellurium to carbon bonds must be excluded. The infrared active carboxylate stretching frequencies are gathered into Table 2 and it is clear, for the three compounds for which solution and solid state spectra could be obtained, that there is no change in tellurium—carboxylate interaction on passing from the solid state to solution. Also, the separation of $\nu_{as}(CO)$ and $\nu_s(CO)$, which can be taken as a measure of the ester like character of the carboxylate group, is very similar to that noted for derivatives of monocarboxylic acids [2]. Hence it is probably legitimate to consider the interaction of tellurium with the carboxylate group similar in, say, the diacetate [2] and the *o*-phthalate derivatives of $R_2Te$. In addition the lack of splitting of the carboxylate vibrations suggests that all four —COO groups are in similar environments within the dimeric molecules, an observation which leads naturally to the suggestion of the alternative structures depicted in Fig. 1.

The $^1H$ NMR spectra of the di(*p*-methoxyphenyl)- and di(*p*-ethoxyphenyl)

TABLE 2

SPECTROSCOPIC DATA FOR SOME DIMERIC ORGANOTELLURIUM PHTHALATES

| Compound | $\nu_{as}(CO)$ ($cm^{-1}$) | $\nu_s(CO)$ ($cm^{-1}$) | ($CH_3$ or $C_2H_5$) [a] | |
|---|---|---|---|---|
| $Ph_2Te(C_8H_4O_4)$ | 1645 (mull) | 1305 (mull) | | |
| | 1640 ($CHCl_3$) | 1305 ($CHCl_3$) | | |
| $(MeOC_6H_4)_2Te(C_8H_4O_4)$ | 1635 (mull) | 1288 (mull) | 7.72(s) | ($CDCl_3$) |
| | 1640 ($CHCl_3$) | 1290 ($CHCl_3$) | | |
| $(EtOC_6H_4)_2Te(C_8H_4O_4)$ | 1640 (mull) | 1300 (mull) | 6.12(q) | 8.74(t) |
| | 1641 ($CHCl_3$) | 1300 ($CHCl_3$) | 8.78(t) | ($CDCl_3$) |
| $Ph_2Te(C_8Br_4O_4)$ | 1660 (mull) | 1265 (mull) | | |
| $(MeOC_6H_4)_2Te(C_8Br_4O_4)$ | 1660 (mull) | 1250 (mull) | | |

[a] Relative to TMS (ppm).

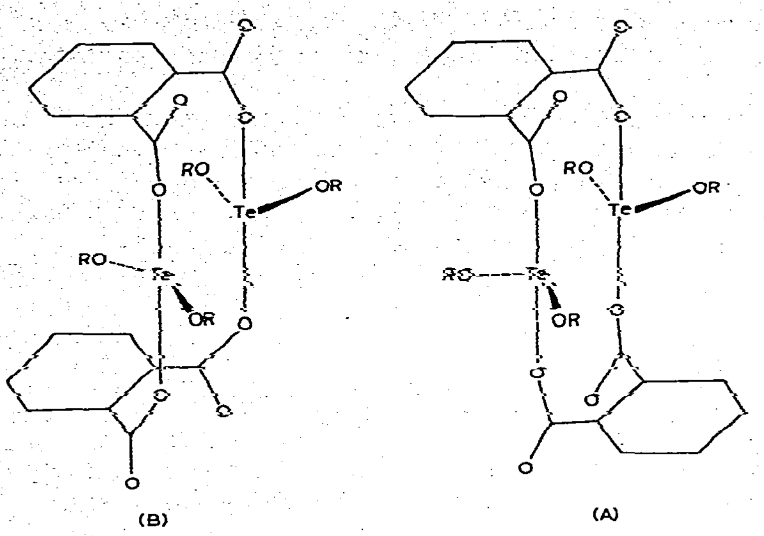

Fig. 1. Proposed structures of diorganotellurium *o*-phthalate.

tellurium *o*-phthalates are helpful in showing the correct ratio of aromatic to aliphatic protons and hence supporting the stoicheiometry and purity of the materials. However, in the case of ($p$-Et$OC_6H_4$)$_2$Te($C_8H_4O_4$) the methylresonance consists of two triplets of 1/1 intensity ratio although no splitting of the methylene resonance is resolved. A possible explanation is that the steric cone swept out by the large $CH_3CH_2O$-group brings the $CH_3$ protons sufficiently close to the aromatic ring of the phthalate for the chemical shift to be marginally affected, thus the observation of two methyl resonances is consistent only with structure B of Fig. 1.

The implication of the structures in Fig. 1 is that the tellurium atoms will be separated by a minimum of 3.6 Å (cf. twice covalent single bond radius 2.54 Å) [5] and thus no strong interaction should be expected, as confirmed by the electronic spectra of the molecules which gave no evidence of strong Te—Te interaction in these compounds.

No pure compounds were isolated from reactions of $R_2TeCl_2$ and the sodium salts of iso- or tere-phthalic acids but tetrabromo *o*-phthalic acid afforded a clean derivative which appears to be the same in all respects to the *o*-phthalates discussed above.

Shaw and co-workers [6] have recently shown that, under some circumstances, very large chelate rings may be stable and indeed the dimeric platinum compounds prepared from $PtCl_2(NCPh)_2$ and t-$Bu_2P(CH_2)_{10}P$-t-$Bu_2$ bear a formal similarity to the phthalate compounds described in this paper. We debated therefore the possibility of bridging the axial positions of the pseudo-trigonal bipyramidal arrangement about diaryltellurium(IV) with an aliphatic dicarboxylate ion since t-$Bu_2P(CH_2)_{10}P$-t-$Bu_2$ does also give a monomeric complex with platinum(II) in which *trans* positions are spanned in a square planar complex by a chelating ligand. For this purpose we chose sebacic acid which, like Shaw's phosphine, could give a thirteen member chelate ring. However reactions between sodium sebacate and diphenyl- and di(*p*-methoxyphenyl)tellurium dichloride obviously failed to afford monomeric compounds. The observed molecular weight was roughly in correspondance with a trimeric formulation but a mixture of molecular species is likely since other workers using a different preparation have obtained higher average molecular weights [4]. Thus in the case of sebacic acid polymer, or oligomer, formation is favoured over chelation.

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