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Triphenyltellurium(IV) dithiocarbamates, xanthates, and dithiophosphates

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Abstract

Ph_3TeCl reacts with a molar equivalent of a sodium dithiocarbamate, xanthate, or dithiophosphate (S–SNa) to give $Ph_3Te(S–S)$ type derivatives. Molecular weight and conductivity measurements in solution suggest that these new triphenyltelluronium compounds are ionized in polar solvents but show a very strong tendency towards ion-association. The IR spectral data suggest that all these sulphur donors are coordinated in the η^1 mode in the new compounds. Their ^1H NMR spectra are characteristic, and are consistent with the monodentate behaviour of the S-ligands. Photolysis of their toluene/benzene/chloroform solutions (~ 1 to 10 mM) gives Ph_2TeO, biphenyl, and disulphide. When O_2 is bubbled through their solutions during photolysis, TeO_2 is also formed. The rates of the UV-promoted decomposition decreases in the order xanthate > dithiocarbamate > dithiophosphate.

Introduction

The chemistry of tellurium(II and IV)-sulphur donor complexes is of interest because tellurium(IV) dithiocarbamates find applications as accelerators in rubber vulcanization [1,2] and many such derivatives have unique structural features [3–7]. Recently tellurium(IV) dithiocarbamates have been found to be very promising as stablizers for polypropene [8]. Of various S-donors [3,4,9], thioureas have been most studied, and coordination of xanthates, dithiocarbamates, and dithiophosphates to the tellurium(II and IV) has received less attention, and reports on organotellurium complexes containing these ligands are scarce [5,7]. The compounds $ArTe(S–S)Cl_2$ and $Ar_2Te(S–S)_2$ (S–S = dithiophosphate) were reported for the first time only very recently by Drake et al. [5]. Since no triphenyltellurium(IV) dithiocarbamate, dithiophosphate, or xanthate appeared to exist, we decided to study them in the hope that some of the resulting compounds might be of value in rubber or polymer technology. In the present paper their synthesis, spectral characteristics, and UV-promoted reactions are described.

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Experimental

Published methods were used for the synthesis of Ph_3TeCl [10] and the sodium salts of *N*,*N*-dimethyl, *N*-methyl, *N*,*N*-diethyl, *N*,*N*-diethanol, pyrrolidine, and morpholine dithiocarbamate [11], methyl, ethyl, n-propyl, i-propyl, i-butyl and cyclohexyl-xanthate [12], and dimethyl, diethyl and diisopropyl-dithiophosphate [13]. Elemental analyses and physical measurements were carried out as describd earlier [14]. For the photolysis experiments a 125 Watt UV lamp was used.

Synthesis of triphenyltellurium(IV) dithiocarbamates

To an aqueous solution of Ph_3TeCl (1.25 mmol) maintained at 60–70 °C, an aqueous solution of sodium dithiocarbamate (1.25 mmol) was added with stirring. The stirring was continued for 30 min, and the precipitate was then filtered off, washed with hot water, dried, and recrystallized from 1/1 $CHCl_3/CH_3CN$, except in case of $Ph_3Te(SC(S)NEt_2)$ for which CH_3CN was used. Yield 68–75%. The m.p. and ^1H NMR (in $CDCl_3$ at 25 °C) and molecular weight data are as follows:

$Ph_3Te(SC(S)NMe_2)$: m.p. 160–162 °C. Analysis: Found: C, 53.25; H, 4.26; N, 2.65; Te, 27.45. $C_{18}H_{21}NS_2Te$ calc.:C, 52.62; H, 4.38; N, 2.92; Te, 26.66%. NMR: δ 3.40 (s, 6H, CH_3), 7.27–7.77 (m, 15H, phenyl). Mol. wt.: Found 483; calc.: 476.8.

$Ph_3Te(SC(S)NHMe)$: m.p. 145–147 °C. Analysis: Found: C, 52.32; H, 4.01; N, 2.53; Te, 26.92. $C_{17}H_{19}NS_2Te$ calc.: C, 51.66; H, 4.09; N, 3.01; Te, 27.44%. NMR: δ 3.0 (d, 3H, *J*(H–H) 5 Hz, CH_3), 7.27–7.79 (m, 16H, phenyl + NH). Mol. wt.: Found: 461; calc.: C, 464.6.

$Ph_3Te(SC(S)NEt_2)$: m.p. 158–160 °C. Analysis: Found: C, 53.81; H, 4.72; N, 2.55; Te, 24.50. $C_{20}H_{25}NS_2Te$ calc.: C, 54.48; H, 4.93; N, 2.76; Te, 25.19%. NMR: δ 1.16 (t, 6H, CH_3), 3.96 (q, 4H, CH_2), 7.27–7.78 (m, 15H, phenyl). Mol. wt.: Found: 495; calc.: C, 506.6.

$Ph_3Te(SC(S)N(C_2H_4OH)_2)$: m.p. 138–140 °C. Analysis: Found: C, 51.42; H, 4.59; N, 2.84; Te, 24.16. $C_{20}H_{25}NO_2S_2Te$ calc.: C, 51.34; H, 4.65; N, 2.60; Te, 23.69%. NMR: δ 3.49 (br, OH), 3.89 (t, 4H, NCH_2), 4.23 (t, 4H, OCH_2), 7.26–7.83 (m, 15H, phenyl). Mol. wt.: Found: 525; calc.: 538.6.

$Ph_3Te(SC(S)\overline{N(CH_2)_2C}H_2)$: m.p. 168–170 °C. Analysis: Found: C, 53.81; H, 4.37; N, 2.58; Te, 26.55. $C_{23}H_{23}NS_2Te$ calc.: C, 54.69; H, 4.56; N, 2.77; Te, 26.29%. NMR: δ 1.87 (t, 4H, CH_2), 3.73 (t, 4H, CH_2N), 7.27–7.79 (m, 15H, phenyl). Mol. wt.: Found: 524; calc.: C, 504.6.

$Ph_3Te(SC(S)\overline{N(CH_2)_2O(C}H_2)_2)$: m.p. 202–204 °C. Analysis: Found: C, 52.56; H, 4.27; N, 2.51; Te, 23.84. $C_{23}H_{23}NOS_2Te$ calc.: C, 53.02; H, 4.42; N, 2.69; Te, 24.51%. NMR: δ 3.59 (t, 4H, CH_2N); 4.25 (t, 4H, OCH_2), 7.26–7.79 (m, 15H, phenyl). Mol. wt.: Found: 510; calc. 520.6.

Triphenyltellurium(IV) xanthates, synthesis

Ph_3TeCl (1.25 mmol) was treated with sodium xanthate (1.25 mmol) as described for triphenyltellurium(IV) dithiocarbamates. The isolated products were recrystallized from acetonitrile. Yield 65–72%. The m.p., elemental analysis, ^1H NMR data (in $CDCl_3$ at 25 °C) and molecular weights are:

$Ph_3Te(SC(S)OMe)$: m.p. 130–132 °C. Analysis: Found: C, 51.44; H, 3.82; Te, 27.90. $C_{20}H_{18}OS_2Te$ calc.: C, 51.55; H, 3.87; Te, 27.41%. NMR: δ 4.01 (s, 3H, OCH_3), 7.27–7.77 (m, 15H, phenyl). Mol. wt.: Found: 468; calc.: 465.6.

Ph$_3$Te(SC(C)OEt): m.p. 128–130 °C. Analysis: Found: C, 51.87; H, 3.99; Te, 27.05. $C_{21}H_{20}OS_2Te$ calc.: C, 52.54; H, 4.17; Te, 26.61%. NMR: δ 1.33(t, 3H, CH_3), 4.46 (q, 2H, OCH_2), 7.27–7.77 (m, 15H, phenyl). Mol. wt.: Found: 491; calc.: C, 479.6.

Ph$_3$Te(SC(S)O(n-Pr)): m.p. 143–145 °C. Analysis: Found: C, 53.06; H, 4.33; Te, 25.57. $C_{22}H_{22}OS_2Te$ calc.: C, 53.48; H, 4.46; Te, 25.35%. NMR: δ 0.95 (t, 3H, CH_3), 1.72 (tq, 2H, CH_2), 4.37 (t, 2H, OCH_2), 7.27–7.77 (m, 15H, phenyl). Mol. wt.: Found: 482; calc. 493.6.

Ph$_3$Te(SC(S)O(i-Pr)): m.p. 146–148 °C. Analysis: Found: C, 52.88; H, 4.32; Te, 24.95. $C_{22}H_{22}OS_2Te$ calc.: C, 53.48; H, 4.46; Te, 25.35%. NMR: δ 1.29, 1.36 (d, 6H, J(H–H) 6 Hz, CH_3), 5.69 (s, 1H, OCH), 7.26–7.77 (m, 15H, phenyl). Mol. wt.: Found 479; calc.: 493.6.

Ph$_3$Te(SC(S)O(i-Bu)): m.p. 154–156 °C. Analysis: Found: C, 53.52; H, 4.66; Te, 24.35. $C_{23}H_{24}OS_2Te$ calc.: C, 54.37; H, 4.73; Te, 25.14%. NMR: δ 0.90 (t, 3H, CH_2CH_3), 1.24, 1.31 (d, 3H, $CHCH_3$), 1.76 (dt, 2H, CH_2), 5.51 (tq, 1H, CH), 7.27–7.78 (m, 15H, phenyl). Mol. wt.: Found: 486; calc.: C, 507.6.

Ph$_3$Te(SC(S)OC$_6$H$_{11}$): m.p. 130–132 °C. Analysis: Found: C, 55.73; H, 4.45; Te, 23.50. $C_{25}H_{26}OS_2Te$ calc.: C, 56.22; H, 4.87; Te, 23.91%. NMR: δ 0.7–2.16 (m, 10H, CH_2), 5.49 (m, 1H, OCH), 7.26–7.77 (m, 15H, phenyl). Mol. wt.: Found: 540; calc.: C, 633.6.

Synthesis of triphenyltellurium(IV) dialkyldithiophosphate

These compounds were prepared in the way described for triphenyltellurium(IV) dithiocarbamates, and were recrystallized from a 1/1 mixture of chloroform and n-hexane. Yield ~ 65%. The m.p., elemental analysis, ^1H NMR data (in $CDCl_3$ at 25 °C) and molecular weights were as follows:

Ph$_3$Te(SP(S)(OMe)$_2$): m.p. 168–170 °C. Analysis: Found: C, 46.85; H, 4.30; Te, 25.09. $C_{20}H_{21}O_2PS_2Te$ calc.: C, 46.55; H, 4.07; Te, 24.75%. NMR: δ 3.45, 3.59 (d, 6H, J(H–H) 15 Hz, OCH_3), 7.27–7.85 (m, 15H, phenyl). Mol. wt.: Found: 509; calc.: 515.6.

Ph$_3$Te(SP(S)(OEt)$_2$): m.p. 160–162 °C. Analysis: Found: C, 48.83; H, 4.01; Te, 24.03. $C_{22}H_{25}O_2PS_2Te$ calc.: C, 48.57; H, 4.59; Te, 23.46%. NMR: δ 1.22 (t, 6H, CH_3); 3.92 (dq, 4H, OCH_2), 7.27–7.81 (m, 15H, phenyl). Mol. wt.: Found: 571; calc.: 543.6.

Ph$_3$Te(SP(S)(O-i-Pr)$_2$): m.p. 150–152 °C. Analysis: Found: C, 50.61; H, 4.4; Te, 21.73. $C_{24}H_{29}O_2PS_2Te$ calc.: C, 50.29; H, 5.06; Te, 22.32% NMR: δ 1.19, 1.25 (d, 12H, CH_3), 4.59 (dsep., 2H, OCH), 7.26–7.80 (m, 15H, phenyl). Mol. wt.: Found: 564; calc.: C, 572.6.

Results and discussion

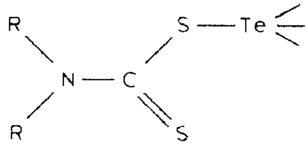
Sodium dithiocarbamates, xanthates, and dithiophosphates (S–SNa) react with Ph_3TeCl according to eq. 1. The resulting triphenyltelluronium derivatives are soluble in common organic solvents. The molar conductances of their millimolar solutions in DMSO and DMF are in the ranges 23–44 and 38–70 ohm^{-1} cm^2 mol^{-1}, respectively. These values indicate that in both solvents their behaviour is very close to that of a 1/1 electrolyte. The molecular weights determined in

$$Ph_3TeCl + (S\text{–}Na) \xrightarrow{50\text{–}60\,°C} Ph_3Te(S\text{–}S) + NaCl \qquad (1)$$

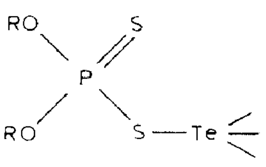
chloroform (concentration 9–17 mg/ml) do not indicate any ionization or polymerization. These observations suggest that the compounds ionize in polar solvents but the propensity for ion-association is very strong, and consequently in less polar solvents and at higher concentration levels they behave virtually as nonelectrolytes. The present derivatives appear to have a greater tendency than other triphenyltelluronium salts towards ion-association [15,16].

IR and NMR spectra

The ν(TeC) band in the IR spectra of all these compounds appears at ca. 250 cm^{-1}. The bands between 280 and 330 cm^{-1} seem to arise from ν(TeS). IR spectra of triphenyltellurium(IV) dithiocarbamates were interpreted after subtraction of the IR bands of Ph_3TeCl from them. The position of ν(CN) (1400–1500 cm^{-1}) is consistent with the recent report about such a band in the spectrum of η^1-dithiocarbamates of cobalt(III) [17] and with other literature reports on the η^1-mode. The two ν(CS) bands (around 1000 cm^{-1}) have a separation of ca. 20–100 cm^{-1}, further supporting the η^1-mode of ligation for these dithiocarbamates, as shown in structure A. In IR spectra of triphenyltellurium(IV) xanthates ν(COC), ν(CO) and ν(CS) appear in the ranges 150–1190, 1075–1120 and 1035–1050 cm^{-1}, respectively, suggesting that these sulphur donors are behaving as monodentate ligand [19,20].



(**A**)



(**B**)

In the ^1H NMR spectra of triphenyltellurium(IV) xanthates and dithiocarbamates the various integration ratios are in agreement with the proposed compositions. The chemical shifts of the alkyl group protons of the dithiocarbamates are close to the values recently reported [17] for other η^1-dithiocarbamates, favouring structure **A**, as implied by the infrared spectra. The ^{13}C NMR spectra of the xanthates and dithiocarbamates are also characteristic, but the C=S signal could not be located.

Triphenyltellurium(IV) dialkyldithiophosphates exhibit ν(P–O(C)), $\nu_{as}(PS_2)$ and $\nu_s(PS_2)$ bands at 920–1010, 640–670 and 540–550 cm^{-1}, respectively, consistent with reports on the unidentate dialkyldithiophosphate [21]. Their ^1H NMR spectra are characteristic, and the OR signals are closer to the similar signals from $Ph_3Sn(SP(S)(OR)_2)$ than to those from $Ph_3Sn(S_2P(OR)_2)$ [21], thus favouring structure **B**.

The existence of a weak interaction between Te and the other uncoordinated sulphur can not be ruled out for the three classes of compounds in the absence of a crystal structure determination, which could not be undertaken owing to our inability to obtain suitable crystals. Nevertheless the chelation of tellurium with two sulphur atoms does not seem to take place in any of them.

Photochemical reactions

The $Ph_3Te(S–S)$ type derivatives decompose when their solutions are irradiated with UV light. Irradiation of the solutions (~ 10^{-2}–10^{-3} M) in toluene/benzene/

chloroform for 5–6 days leads to complete decomposition. Three products identified after photolysis under ambient conditions were Ph_2TeO, Ph_2, and the disulphide. Probably eq. 2 represents the major reaction (~ 70%) involved in the photolysis.

$$2Ph_2Te(S\text{–}S) + O_2 \rightarrow 2Ph_2TeO + (S\text{–}S)_2 + Ph_2 \qquad (2)$$

When a stream of oxygen is bubbled through the solution during the photolysis, TeO_2 is formed as an additional product and rate of the reaction is somewhat increased. The rate of photochemical decomposition of these triphenyltelluronium compounds increases in the order xanthate > dithiocarbamate > dithiophosphate. A brown semi-solid product containing elemental tellurium is also formed in both the reaction, but we have been unable to identify the other components.

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