The Structure of a Stable New Organotellurium Azide: Bis-Azidodiphenyltellurium(IV) Oxide

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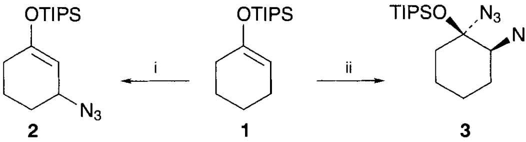
Diphenyltelluroxide reacts with azidotrimethylsilane to give a remarkable stable adduct $(Ph_2TeN_3)_2O$ which was characterised by X-ray crystallography.

The syntheses of the β-azido product **2** or the 1,2-bisazido product **3** from the triisopropylsilyl (TIPS) enol ether **1** are new and useful reactions for the introduction of nitrogen into synthetic intermediates, Scheme 1.[1,2] We have speculated that the reactive hypervalent iodine reagent is either **4** or **4a** but because of their instability they have not been isolated or characterized, eqn. (1). Above −20 °C the intermediates smoothly decompose into iodobenzene, dinitrogen and hexamethyl disiloxane. A more stable azidonation reagent derived from *o*-iodosobenzoic acid has been reported, and this may be more amenable to structural studies.[3,4]

We have already suggested that this reaction pathway may be a general one and that other elements (M) may be suitable replacements for iodine, eqn. (2).[5] Ideally these new reagents will possess a more convenient reactivity/stability profile. To this end it was found that Ph_2SeO, Ph_3AsO and Ph_3PO were cleanly reduced to Ph_2Se, Ph_3As and Ph_3P [and $(Me_3Si)_2O$ and N_2], respectively when treated with Me_3SiN_3 at −20 °C. When conducted in the presence of the TIPS enol ether **1** no azidonation occurred. Selenium, arsenic and phosphorous have stable hypervalent oxidation states compared to lower ones which may explain why no oxidation products are observed. However, the fifth row of elements in the periodic table have less stable hypervalent oxidation states and are correspondingly more reactive.[6] With this in mind it was decided to examine diphenyltelluroxide. The reduced diphenyltelluride would have the added advantage of being oxidised by air or hydrogen peroxide, thus allowing for a potential catalytic cycle.[7]

Diphenyltelluroxide was treated with azidotrimethylsilane in dichloromethane at room temperature, Scheme 2. No nitrogen gas was evolved. After three hours, evaporation of solvent yielded a mixture of two products **5** and **6**. The mixture was heated without solvent under high vacuum to 100 °C for two hours to drive conversion of **5** to **6** to completion. Crystallisation from dichloromethane and diethyl ether afforded pure bisazidodiphenyltellurium(IV) oxide, **6** (92% yield) as white needles.†



Scheme 1 *Reagents and conditions*: i, PhIO (1.5 equiv.), $TMSN_3$, CH_2Cl_2; ii, i + TEMPO (10%), −40 °C. (TIPS = $SiPr^i_3$)

Crystals of **6** were suitable for X-ray diffraction studies, Fig. 1.‡ The compound belongs to the known class of oxides $(R_2TeX)_2O$[8] and shares the same crystal structure as the isothiocyanate $(Ph_2TeNCS)_2O$, the only previous structure in

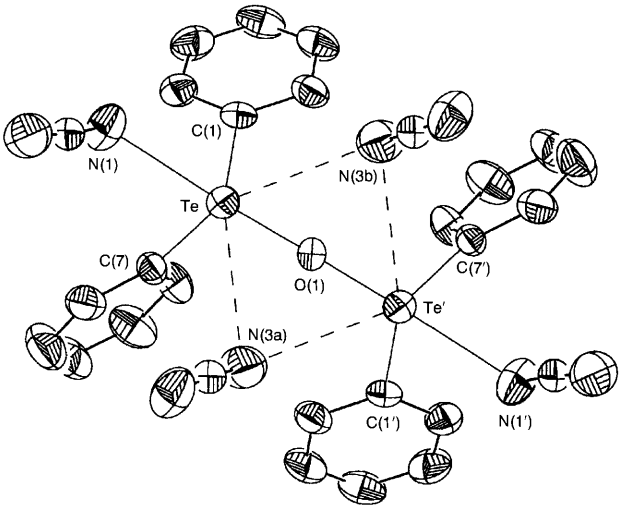
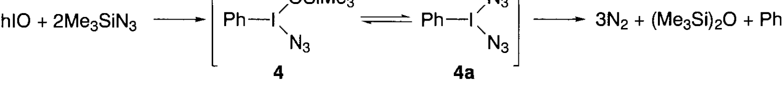
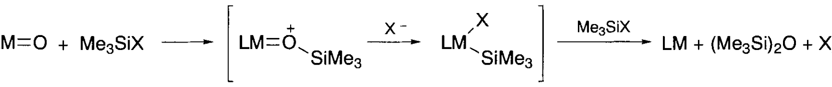


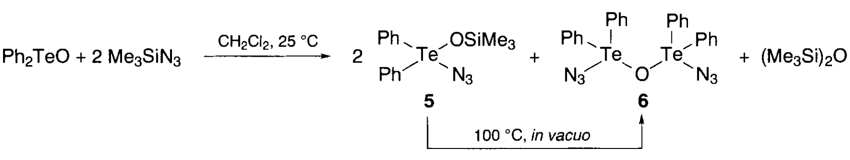
Fig. 1 View of the Te complex **6** with a partial atom labelling scheme. The view direction is approximately along the twofold rotation axis. The coordination about Te is distorted octahedral. The dashed lines indicate the long secondary Te–N bonds. Important bond lengths (Å) and angles (°): Te–C(1) 2.088(8), Te–C(7) 2.123(7), Te–O(1) 1.972(3), Te–N(1) 2.397(8), Te–N(3a) 3.137(9), Te–N(3b) 3.173(9), Te–O(1)–Te 126.2(4), Te–N(3a)–Te′ 67.7(3). Atoms labelled with ′ are related by 1 − *x*, *y*, 3/2 − *z*. N(3a) is related to N(3) by 1 − *x*, 1 − *y*, 1 − *z* and N(3b) is related to N(3) by *x*, 3/2 − *y*, 1/2 + *z*. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms have been omitted for clarity.



$$PhIO + 2Me_3SiN_3 \longrightarrow \left[\underset{\mathbf{4}}{Ph{-}I(OSiMe_3)(N_3)} \rightleftharpoons \underset{\mathbf{4a}}{Ph{-}I(N_3)_2} \right] \longrightarrow 3N_2 + (Me_3Si)_2O + PhI \quad (1)$$



$$LM{=}O + Me_3SiX \longrightarrow \left[LM{=}\overset{+}{O}{-}SiMe_3 \xrightarrow{X^-} LM(X)(OSiMe_3) \right] \xrightarrow{Me_3SiX} LM + (Me_3Si)_2O + X_2 \quad (2)$$



$$2\,Ph_2TeO + 2\,Me_3SiN_3 \xrightarrow{CH_2Cl_2,\ 25\ °C} 2\,\underset{\mathbf{5}}{Ph_2Te(OSiMe_3)(N_3)} + \underset{\mathbf{6}}{(N_3)Ph_2Te{-}O{-}TePh_2(N_3)} + (Me_3Si)_2O \quad (3)$$

this class to have been determined.[9] The azide **6** $(Ph_2TeN_3)_2O$ is unusually thermally stable (mp 174–176 °C, without decomposition, gas evolution occurs at 200 °C) a property that has also been observed for triphenyltellurium azide (mp 155.5–156.5 °C).[10] In our case the high stability may, in part, be attributed to the secondary bonding interactions between the tellurium atom and the more distant azide group from another molecule of $(Ph_2TeN_3)_2O$.

In attempts to conduct 1,3-dipolar cycloaddition chemistry, **6** was treated with dimethyl acetylenedicarboxylate at 25 °C. The only identifiable product was diphenyl telluride, with the remaining mass balance consisting of unidentifiable mixtures and unreacted **6**.

In conclusion, a new organotellurium azide **6**, has been prepared and its structure determined by X-ray crystallography. It is unusually thermally stable (*cf.* $PhIO/Me_3SiN_3$ mixtures only stable below 0 °C) and so far has proved resistant to useful chemical transformations.

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Footnotes

† *Selected data* for 6: mp 174–176 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92–7.64 (8 H, m), 7.58–7.38 (12 H, m); IR (thin film) ν 2025 cm^{-1}, ($CHCl_3$ soln.) ν 2040 cm^{-1}.

‡ *Crystal data* for **6**: thin colourless plate-like crystals of **6** ($C_{24}H_{20}N_6OTe_2$) were grown by slow evaporation from a dichloromethane–diethyl ether solution. Crystals were monoclinic, space group $C2/c$ (No. 15), a = 18.202(2), b = 12.966(2), c = 11.172(2) Å, β = 105.90(1)°, V = 2538.8(7) Å^3, Fw = 663.66, $F(000)$ = 1272, μ = 23.28 cm^{-1}, D_c = 1.74 g cm^{-3}, Z = 4. The molecule lies on a crystallographic two fold rotation axis at 1/2, y, 3/4 passing through the bridging oxygen atom. 2923 unique data were collected at room temp. using ω-scans on a Siemens P4 diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS, G. M. Sheldrick, 1992) and refined on F^2 (SHELXL, G. M. Sheldrick, 1993) to an $R_w(F^2)$ = 0.145, with a corresponding conventional $R(F)$ = 0.0545. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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