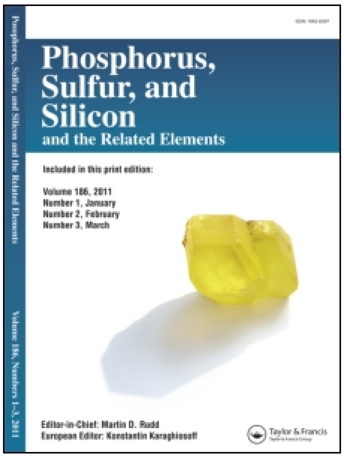

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Mont, W. W. Du , Hensel, R. , Kubiniok, S. , Lange, L. and Severengiz, T.(1988) 'NOVEL REACTIONS WITH TELLURIUM AND ORGANOTELLURIUM REAGENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 38: 1, 85 — 95

To link to this Article: DOI: 10.1080/03086648808079704

URL: http://dx.doi.org/10.1080/03086648808079704

Phosphorus and Sulfur, 1988, Vol. 38, pp. 85–95
Reprints available directly from the publisher

NOVEL REACTIONS WITH TELLURIUM AND ORGANOTELLURIUM REAGENTS

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Abstract Novel reactions of elemental tellurium, organic ditellurides and diselenides and or reagents with Te-Li, Se-Li and Te-Si bonds are reviewed. These reagents have been used to prepare new molecules with Te-P, Se-P, Te-C, Te=C, Te-I and Se-I bonds.

For more than ten years the Lawesson Reagent has been known to be a powerful agent for the transformation of C=O into C=S groups. A comparable reagent for the conversion of C=O to C=Se or C=Te groups has not yet been described. In fact, even simple binary tellurides of phosphorus have not been satisfactorily characterized.

PHOSPHANE TELLURIDES

Early work by Zingaro [1] showed, that certain teriary phosphanes nucleophilically degrade elemental tellurium and form tertiary phosphane tellurides, R_3PTe. These compounds are much less stable than phosphane oxides, sulfides and selenides. The most remarkable property of phosphane tellurides is their kinetic lability with respect to tellurium transfer to non-coordinated phosphanes. These rapid P^{III}/P^{V} redox reactions by tellurium transfer are initiated by nucleophilic attack of the phosphorus lone pair at tellurium leading to transition states with hypervalent (10-Te-2)-configuration [2].

$$R_3P + 1/x\ Te_x \rightleftharpoons \underset{\underline{1}}{R_3PTe} \qquad (1)$$

$$R_3P{=}\ddot{\underset{\cdot\cdot}{Te}} + :\overset{*}{P}R_3 \rightleftharpoons R_3P: + \ddot{T}e{=}\overset{*}{P}R_3 \qquad (2)$$

With tri-n-butylphosphane reaction (1) does not go to completion when equimolar amounts of phosphane and tellurium are used. A twofold excess of the phosphane is necessary to "dissolve" elemental tellurium. Tri-t-butylphosphane, a much stronger reducing agent and/or σ-donor reacts with an equimolar amount tellurium to give a remarkably stable, but still kinetically labile, phosphane telluride $\underline{1}$.

TELLUROPHOSPHANES

Tellurium transfer reactions between tertiary phosphanes are special cases of rapid P^{III}/P^{V} redox reactions, but they cannot serve as appropriate models for the interaction of elemental phosphorus with elemental tellurium. They key step of the interaction of phosphorus rings and cages with tellurium chains will be the insertion of Te atoms into P-P bonds, just like the insertion of oxygen and sulfur atoms into P_4 give P_4O_6 and P_4S_3, respectively.

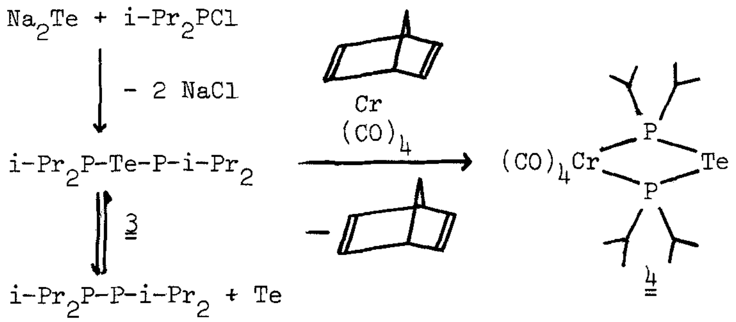
Thus, a suitable model for the interaction of elemental tellurium with phosphorus is the tellurium atom insertion into P-P bonds leading to P^{III}-Te-P^{III} moieties. This reaction may proceed with Te atoms that were derived from nucleophilic degradation of elemental tellurium with help of the phosphorus lone pair (see eqn. 1), or by "direct" interaction of tellurium chains with phosphorus-phosphorus bonds in a kine of (2+2)dismutation reaction with subsequent rearrangements.

The insertion of a Te atom into a P-P bond was first observed, when tetra-t-butyldiphosphane was heated with Te powder in boiling toluene (eqn. 3a).

$$\text{t-Bu}_2\text{P-P-t-Bu}_2 + \text{Te} \longrightarrow \underset{\mathbf{2}}{\text{t-Bu}_2\text{P-Te-P-t-Bu}_2} \qquad (3a)$$

$$\text{i-Pr}_2\text{P-P-i-Pr}_2 + \text{Te} \rightleftharpoons \underset{\mathbf{3}}{\text{i-Pr}_2\text{-Te-P-i-Pr}_2} \qquad (3b)$$

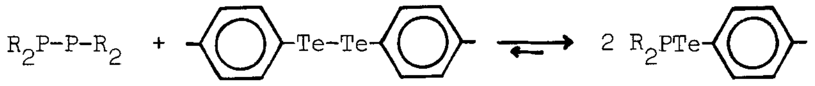
Tellurobis(di-t-butylphosphane) 2, a stable compound, was obtained in quantitative yield. Tetra-i-propyldiphosphane reacts with tellurium under milder conditions but not quantitatively (eqn. 3b). Diphosphane/tellurobisphosphane mixtures are always obtained. Tellurobis(di-i-propylphosphane) prepared from sodium telluride and chlorodi-i-propylphospahne precipitates Te and establishes equilibrium (3b). For this spontaneous detelluration phosphorus lone pairs have to be chemically available. When the P lone pairs are made unavailable, for instance, by coordination to tetracarbonylchromium acceptors, the tellurobisphosphane is kinetically stabilized (eqn. 4).



(4)

Elemental tellurium exists as infinite chains with di-coordinate tellurium. To model the interaction of tellurium chains with phosphorus chains, rings and cages we chose di-p-tolylditelluride as a simple molecular compound which contains just one tellurium-tellurium single bond. Similarly, tetra alkyl diphosphanes obtain just one P-P single bond, and may serve as crude models of elemental phosphorus.

Tetraalkyldiphosphanes react with diaryl ditellurides by a (2+2)dismutation to form (arylteiluro)dialkylphosphanes 5 (eqn. 5). As in the case of the reaction between Te and tetraalkylphosphanes, bulky alkyl groups favor also the formation of the tellurophosphanes in equilibria with ditellurides (eqn. 5).

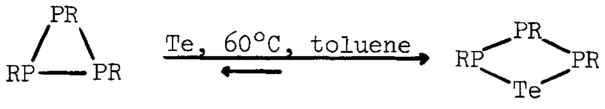


(5)

R = t-Bu, i-Pr

Again, coordination of the P lone pair leads to kinetic stabilisation of the P-Te bond, i.e., the barrier of energy for re-dismutation is raised significantly: The tungsten(0)complex $W(CO)_5$-$P(i\text{-}Pr)_2Te\text{-}C_6H_3\text{-}CH_3$ is completely stable with respect to re-dismutation to di-p-tolylditelluride and a diphosphane-bridged dinuclear complex.

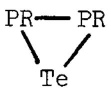
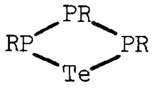
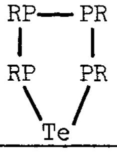
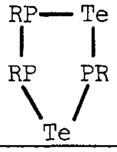
Tetra-t-butyl-cyclotetraphosphane does not react with elemental tellurium even in boiling toluene. However, tri-t-butylcyclotriphosphane inserts at 60°C one tellurium atom into one of the P-P bonds to form a telluratriphosphetane. Cyclotriphosphane with tellurium in boiling toluene produces a mixture of telluracyclophosphanes $(t\text{-}BuP)_xTe_y$ (see Tab. I). These heterocycles are also formed from t-butyldichlorophosphane and bis(trimethylsilyl)telluride or from t-butyl-bis(trimethylsilyl)phosphane and elemental tellurium [4].



(6)

7a

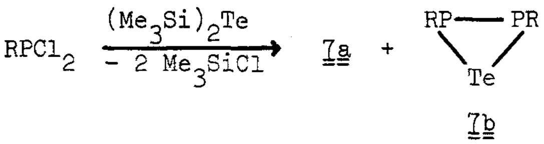
Table I Spectroscopic data for Telluracyclophosphanes

				
MS m/z*	306	394	482	520
δP-31	-70.9	-4, -60 J(PP) 173	+94.8, +89.9 |J(PP)| 319.2 334, 12.4, 5.6 [calc. AA'BB' spectrum]	+100, +154 J(PP) ± 26
δTe-125	-696(t)	-361(d,t)	ca. +378(m)	ca. +586(m)
$J(^{125}Te,^{31}P)$	+226	±84, ±10.7		

* for molecular ion

$\delta^{31}P$: ppm rel. to 85 % H_3PO_4

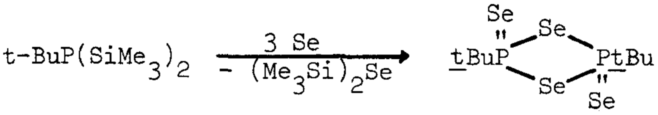
$\delta^{125}Te$: ppm determined rel. to di-p-tolyl ditelluride, values given calc. with δ (rel. Me_2Te) = [δ (rel. Tol_2Te_2) +428 ppm]



(7)

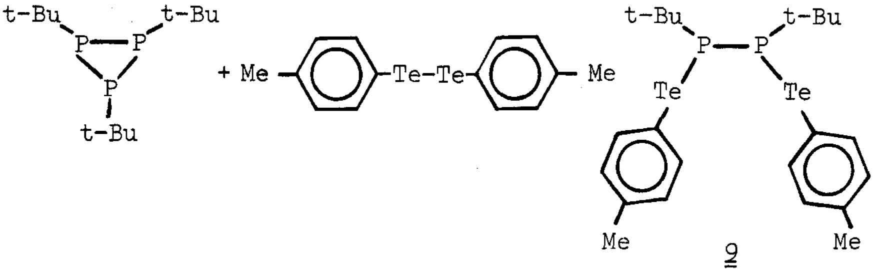
$$RP(SiMe_3)_2 \xrightarrow[-\ (Me_3Si)_2Te]{Te,\ 25^\circ C} \underline{\underline{7a}} \qquad (8)$$

The Te-P heterocycles, $(t\text{-}BuP)_xTe_y$, contain at least one P-P bond and no terminal P=Te function. A P=Te group is not formed even when an excess of tellurium is present in the reaction mixtures.



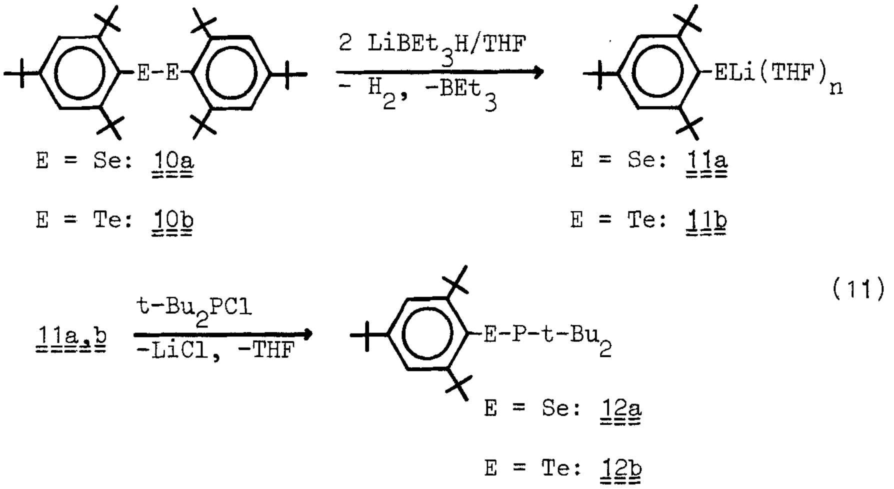
(9)

In contrast with tellurium, selenium converts t-butylbis(trimethylsilyl)-phosphane to the "seleno-Lawesson"-type compound, $[t\text{-}BuPSe_2]_2$ 8 (eqn. 9). Although tetra-t-butylcyclotetraphosphane does not react with di-p-tolyl ditelluride even in boiling toluene, tri-t-butylcyclotriphosphane and di-p-tolylditelluride form - with P-P bond cleavage - 1,2-di-t-butyl-1,2-di(p-tolyltelluro)diphosphane 9 (eqn. 10) at 25°C.



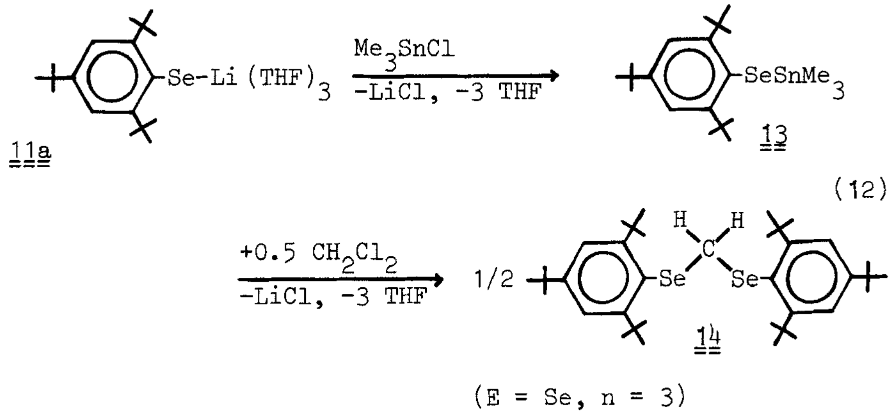
(10)

Compound 9 was isolated in the pure state in the form of yellow crystals. A similar (2+2)dismutation was not observed in reactions between cyclotriphosphane or tetra-t-butyldiphosphane and the bulky bis(2,4,6-tri-t-butylphenyl)ditelluride or bis(2,4,6-tri-t-butylphenyl)diselenide. To attach very bulky 2,4,6-tri-t-butylphenyl-seleno- and -telluro substituents to phosphorus, metal halide elimination reactions have to be carried out. The starting materials are obtained by "superhydride" reduction of the Se-Se or Te-Te bonds.



(11)

The lithium areneselenolate, the structure of which was determined by X-ray diffraction (Se-Li 257.3 pm, CSeLi 103°), is a good reagent for the formation of selenium-carbon and heteroatom bonds (eqn. 12).

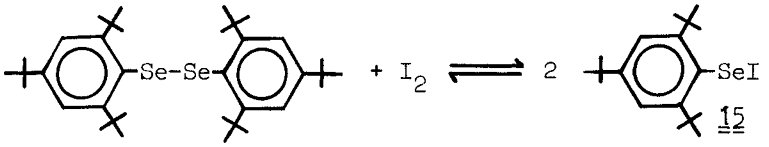


(12)

Bis(2,4,6-tri-t-butylphenyl)ditelluride **10b** allowed the determination of the barrier of enantiomeric interconversion (probably Te-Te bond rotation). The molecular point group C_2 was confirmed by X-ray diffraction data for the ditelluride **10b** [5]. In solution the barrier of 9.9 kcal mol^{-1} for **10b** (determined by dynamic n.m.r.) is significantly lower than the barriers for the corresponding disulfide and diselenide (16.2 and 12.5 kcal mol^{-1}). Steric effects should also be responsible for the low reactivity of the diselenide and the ditelluride towards P-P bonds. It is reasonable to assume that steric crowding disfavors the four-centered transition states necessary for (2+2)dismutation reactions.

COMPOUNDS WITH Se-I BONDS

This concept of kinetic stabilisation led us to the characterization of the first well defined, uncharged molecular compound with a selenium iodine bond. Elemental Se and I are of similar electronegativity, and do not form inorganic binary compounds as do tellurium and phosphorus. Diphenyl diselenide reacts with iodine to give "PhSeI", but n.m.r. data obtained with solutions of "PhSeI" do not allow for a determination of whether PhSeI contains a covalent Se-I single bond or should be formulated as a charge-transfer adduct such as PhSeSePh • 2 I_2. Addition of less than the equimolar amount of iodine to PhSeSePh leads to changes of ^{1}H- and ^{13}C-n.m.r. shifts, but separate signals for PhSeSePh and PhSeI were not observed. However, the bis(2,4,6-tri-t-butylphenyl)diselenide/iodine reaction establishes a dismutation equilibrium (eqn. 13). The dismutation is not rapid on the n.m.r. time scale [6]. Crystallisation afforded pure solid "ArSeI" 15. X-ray diffraction data gave an Se-I distance of 252 pm (shorter than Se-Li 257.3), and the angle CSeI of 97.5°.



(13)

REACTIONS OF BIS(TRIMETHYLSILYL)TELLURIDE WITH ACYL HALIDES

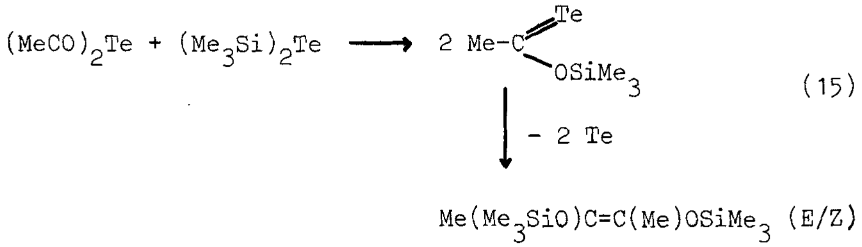
The unavailability of a telluro-Lawesson reagent led us to seek the application of bis(trimethylsilyl)telluride as a precursor for the formation of molecules with C=Te double bonds.

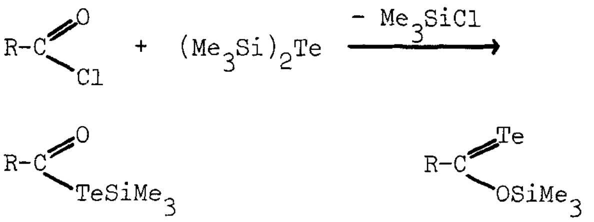
Te-Si bond cleavage of bis(trimethylsilyl)telluride with acyl halides may be used to prepare bis(acyl)tellurides under mild conditions [7]. Thus, diacetyl telluride is formed from bis(trimethylsilyl)telluride and two equivalents of acetyl chloride. However, the reaction of the same disilyl telluride with only one equivalent of acetyl chloride, surprisingly, resulted in an acyloin-type coupling. The reaction mixture is intensely blue. Mass spectroscopy identified trimethylsilyl telluroacetate 16B (R = CH_3) as a thermally labile intermediate. This telluronoester decomposed at room temperature by spontaneous detelluration with formation of (E)- and (Z)-isomers of the corresponding disilyl enediol ether (eqn. 14, 15).

To obtain more detailed information about the properties of silyl tellurocarboxylates, we attempted to isolate a thermally stable compound of this type.

The reaction of pivaloyl chloride with an equimolar amount of bis(trimethylsilyl)telluride in the absence of a solvent produces a blue liquid that contains trimethylsilyl telluropivalate 16 (R = t-C_4H_9) and chlorotrimethylsilane. Removal of the silane by keeping the reaction mixture at 10 mbar for three hours provides a high yield of pure 16 as a blue liquid that is very sensitive to air and moisture but thermally stable at room temperature [8].

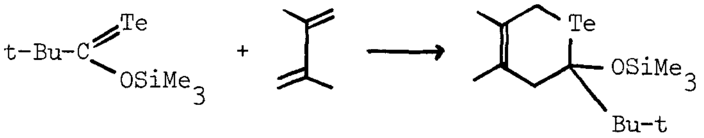
$$MeCOCl + (Me_3Si)_2Te \longrightarrow Me_3SiCl + Te + 1/2\ Me(Me_3SiO)C{=}C(Me)OSiMe_3\ (E/Z) \qquad (14)$$


(15)


16A 16B R = t-Bu

(16)

In contrast to trimethylsilyl thiopivalate, which exists exclusively as the C=S-bonded thiono isomer, the telluro-ester 16 as the neat liquid or in C_6D_6 solution contains the C-Te-Si and the C=Te isomers (65 % 16B, 35 % 16A) as determined by multinuclear n.m.r. spectroscopy. ^1H-n.m.r. spectra indicate that two different species with trimethylsilyl groups and t-butyl groups are present in pure 16. In the ^{13}C-spectra two resonances are present in the carbonyl region. The signal at +207.5 ppm has to be assigned to the silyl telluroacetate 16A, and the resonance at +251.2 to the silyl telluronoacetate. The ^{13}C nucleus is far more deshielded in the C=Te than in the C=O group (compare δ ^{13}C +229.38 for $Bu^t\underline{C}(=Te)OCH_2Bu^t$ [9]). The ^{125}Te-n.m.r. signal of the C=Te group in 16B (+1419 ppm) appears 1190 ppm to low field from isomer 16A (δ +229 ppm), the resonance, which is close to the average of the shifts of $(Me_3Si)_2Te$ (δ ^{125}Te -858) and $(t\text{-}BuCO)_2Te$ (δ ^{125}Te +936). As in the case of compounds with C=Se double bonds, the low field ^{13}C- and ^{125}Te resonances of 16B coincide with a rather small average excitation energy (16B: λ_{max} 624 nm). The 1,3 sigmatropic rearrangement 16A ⇄ 16B is slow on the n.m.r. time scale, but chemical reactions, that we carried out with 16, always proceeded with consumption of both isomers. The reaction of 16 with pivaloyl chloride produces quantitatively di(pivaloyl) telluride and chlorotrimethylsilane. (2+4)cycloaddition reactions of the C=Te double bond of 16B with cyclopentadiene or 2,3-dimethylbutadiene lead to new cyclic telluroacetals (eqn. 17).



(17)

The existence of a 1:2 equilibrium of 16A and 16B which are related by a 1,3-trimethylsilyl shift, indicates, that the strong affinity of silicon for oxygen, which favors C=S and C=Se bonds in silyl thio- or selenocarboxylates, is not sufficient to provide the rather high energy that would be needed for the quantitative formation of a C=Te double bond.

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