

# Synthetic Applications of Organotellurium Chemistry

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Tellurium, classified in group 16<sup>73</sup> of the periodic table of the elements, was discovered in 1782 by the Austrian chemist F. J. Müller von Reichenstein. Its existence was first observed in ores mined in the gold districts of Transylvania, and the mineral was considered to be a type of alloy of bismuth and antimony. Several years later M. H. Klaproth, another Austrian chemist, concluded that the metal had unique properties. He named the newly discovered element tellurium, derived from the latin *tellus*, meaning earth.

Organic tellurium compounds have a history dating back to 1840 when Wöhler prepared dialkyl tellurides, the first organic compounds of tellurium. Since that time an ever increasing number of classes of organotellurium compounds have been described. This work includes synthesis as well as chemical, physical, and structural studies and a comprehensive spectral documentation. Several excellent reviews are now available on the topic.<sup>1-4</sup>

Initially, much of the tellurium work was pursued as an extension of selenium chemistry. However, it soon became clear that there are many dissimilarities in the chemical behavior of the two elements. The period since 1970 has seen a great renaissance in organoselenium chemistry. A major reason for this was the discovery and development of new types of selenium reagents which have proven to be useful and versatile tools in organic synthesis.<sup>5-7</sup> However, little has appeared regarding attempts to develop tellurium-containing reagents of possible utility in organic synthesis.<sup>4,8,9</sup>

This reluctance to work with tellurium may in part be due to the historically bad reputation of organotellurium compounds as being sensitive to air and light, foul-smelling, and difficult to handle. It has even been suggested that manipulations of organotellurium compounds should be carried out in a photographic dark-room containing no light source other than a red safety lamp.<sup>10</sup> In our experience an overwhelming majority of organotellurium compounds can be handled in the laboratory without any special precautions. However, a few classes of compounds (e.g., alkyl, benzyl, or allyl tellurides) are inherently unstable. In those particular cases the use of a red safety lamp may be advisable.<sup>11</sup>

Concerning the odor problem, organotellurium compounds are no worse than their respective organosulfur or organoselenium analogues. Divalent organotellurium compounds containing less than seven or eight carbon atoms may have a rather penetrating odor. These compounds should be handled in a well-ventilated hood.

Lars Engman was born in Bålsta, Uppland, Sweden, in 1952. He received his Ph.D. from the Royal Institute of Technology, Stockholm, in 1980, spent a year of postdoctoral work with Professor M. P. Cava at the University of Pennsylvania, and then joined the faculty at the Royal Institute of Technology. His major research interests are the development of new selective organic transformations based on tellurium, selenium, and sulfur chemistry.

Many organotellurium compounds are highly crystalline or can be readily converted into highly crystalline derivatives. Consequently, these materials are easy to purify and handle.

Toxicity data on organotellurium compounds are sparse; however, the few studies made indicate that organotellurium compounds are less toxic than their selenium counterparts. Hence, there are no major a priori disadvantages of organotellurium chemistry that should deter the organic chemist from exploring its synthetic possibilities. The period since 1980 has seen an increasing activity in the search for synthetic applications of organotellurium chemistry. It is the intention of this Account to highlight some of this work.

Applications of organotellurium chemistry in synthesis can be conveniently divided into carbon-carbon bond-forming reactions and various types of functional group interconversions. Most applications involve an isolable organotellurium compound containing a weak carbon-tellurium bond which is subsequently manipulated into other types of functionalities. In other cases the organotellurium compound occurs as an unstable reaction intermediate. There are also examples of processes that are catalytic with respect to tellurium or an organotellurium reagent.

## Carbon-Carbon Bond-Forming Reactions

Tellurium is surprisingly easily introduced into a variety of organic substances. Many aromatic compounds undergo electrophilic aromatic substitution with tellurium tetrachloride, TeCl<sub>4</sub>, to yield diaryltellurium dichlorides (1). These compounds can be converted in high yields into symmetrical biaryls by treatment with degassed Raney nickel in high-boiling ether solvents<sup>12</sup> (eq 1).

A similar aryl-aryl coupling was achieved starting from an aryltellurium trichloride<sup>13</sup> (2 → 2',2'-dinaphthyl)

(1) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974. See also: Irgolic, K. J. *J. Organomet. Chem.* 1975, 103, 91; 1977, 130, 411; 1978, 158, 235; 1978, 158, 267; 1980, 189, 65; 1980, 203, 367.

(2) Cooper, W. C. "Tellurium"; Van Nostrand-Reinhold Co.: New York, 1971.

(3) Sadekov, I. D.; Bushkov, A. Ya.; Minkin, V. I. *Russ. Chem. Rev. (Engl. Transl.)* 1979, 48, 343.

(4) Petragmani, N.; Comasseto, J. V. In "Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium"; Berry, F. J., McWhinnie, W. R., Eds.; The University of Aston in Birmingham, 1983; p 98.

(5) Clive, D. L. J. *Tetrahedron* 1978, 34, 1049.

(6) Reich, H. J. *Acc. Chem. Res.* 1979, 12, 22.

(7) Liotta, D. *Acc. Chem. Res.* 1984, 17, 28.

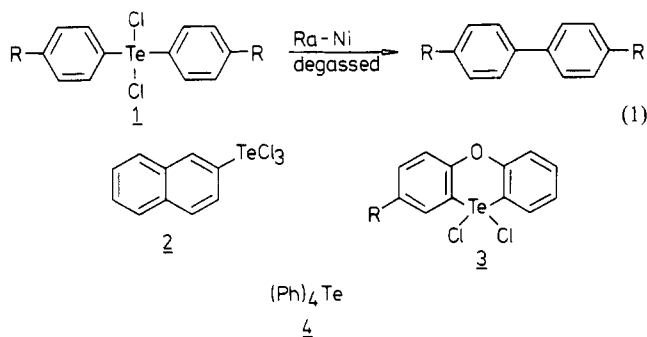
(8) Ley, S. V. *Annu. Rep. Prog. Chem. Sect. B* 1980, 77, 233.

(9) Uemura, S. *Yuki Gosei Kagaku Kyokaishi* 1983, 41, 804.

(10) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* 1980, 102, 4438.

(11) Spencer, H. K.; Cava, M. P. *J. Org. Chem.* 1977, 42, 2937.

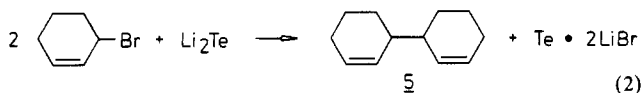
(12) Bergman, J. *Tetrahedron* 1972, 28, 3323. Bergman, J.; Carlsson, R.; Sjöberg, B. *Org. Synth.* 1977, 57, 18.



or a phenoxatellurine<sup>14</sup> (compounds **3** afforded dibenzofuran derivatives via intramolecular C-C bond formation). All these nickel-induced detelluration reactions probably involve aryl radicals. Attempts to couple unsymmetrical diaryltellurium dichlorides resulted in the formation of symmetrical biaryls as the main products.

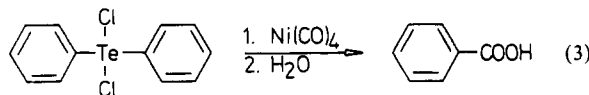
The thermal decomposition of tetraaryltellurium species has also found some use for the synthesis of biaryls. Tetraphenyltellurium (**4**) afforded a quantitative yield of biphenyl and diphenyl telluride when heated in toluene at 140 °C.<sup>15</sup> A mechanistic study of this reaction favored a concerted decomposition process which did not involve radicals.

The thermal extrusion of elemental tellurium from divalent organotellurium species has been successful only when very labile (allylic,<sup>16</sup> benzylic<sup>17</sup>) carbon-tellurium bonds were involved. Clive and co-workers<sup>18</sup> have developed a synthetically useful method for the synthesis of 1,5-dienes based on a tellurium-induced allylic coupling. An allylic halide (exemplified by 3-bromocyclohexene in eq 2) was heated under reflux with



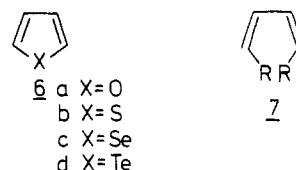
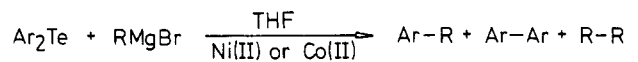
lithium telluride for 1 h in a mixture of dioxane and tetrahydrofuran to afford diene **5** in good yield as a mixture of diastereomers. A mechanistic study has established that bis allylic tellurides are involved as the source of allylic radicals.

Diphenyltellurium dichloride and other aryltellurium species were converted in fair yields to benzoic acid derivatives upon treatment with nickel carbonyl<sup>19</sup> (eq 3). A similar carbonylation reaction also occurred with



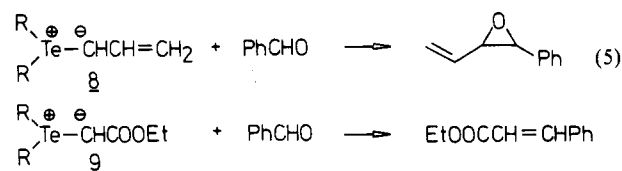
pressurized carbon monoxide in the presence of a stoichiometric amount of a palladium(II) salt.<sup>20</sup> By the

use of transition metals the organic part of various organotelluriums have been attached to other organic moieties such as olefins<sup>21,22</sup> and Grignard reagents.<sup>23</sup> The transition-metal-assisted arylations of olefins are usually, but not always,<sup>22</sup> stoichiometric. However, the modest yields and the formation of complex isomer mixtures has restricted its synthetic utility. Cross-coupling reactions of aryl and alkyl Grignard reagents with organic tellurides can be performed by using a catalytic amount of a Ni, Co, or Pd salt. Unfortunately the product is always contaminated by symmetrical coupling products as shown in eq 4.<sup>23</sup>



When the coupling reaction (RMgBr) was applied to tellurophene (**6d**), good yields of 1,4-disubstituted buta-1,3-dienes **7** were obtained, mostly with retention of configuration.<sup>24</sup> The tellurium compound gave the best results out of all the different heterocycles tried (**6a-d**).

Sulfonium ylides have been frequently employed in organic synthesis for the construction of new carbon-carbon bonds. Their tellurium counterparts, telluronium ylides, had not found any use in synthesis until very recently when Osuka prepared dialkyltelluronium allylides (**8**)<sup>25</sup> and dialkyltelluronium carbethoxymethylides (**9**).<sup>26</sup> The different behavior of these ylides toward carbonyl compounds is demonstrated in the following example. Ylide **8** afforded an  $\alpha,\beta$ -unsaturated epoxide (mainly *Z*) with benzaldehyde whereas ylide **9** produced an  $\alpha,\beta$ -unsaturated carboxylic ester (*E/Z* > 50/1) in good yield (eq 5). Apparently the outcome of



the reaction is highly dependent on the stability of the telluronium ylide. Future research in this area will hopefully serve to define the full synthetic potential of these reactions.

During a study of the oxidizing properties of tellurium dioxide (vide infra) it was found that certain alkyl aromatic compounds (e.g., toluene) were acetoxy-methylated instead of oxidized at the side chain<sup>27,28</sup> (eq

(13) Bergman, J.; Engman, L. *Tetrahedron* 1980, 36, 1275.

(14) Bergman, J. *Chem. Scr.* 1975, 8A, 116. Bergman, J. "Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium", Eds. Berry, F. J.; McWhinnie, W. R. The University of Aston in Birmingham 1983; p 215.

(15) Glover, S. A. *J. Chem. Soc., Perkin Trans. 1* 1980, 1338.

(16) Cuthbertson, E.; MacNicol, D. D. *J. Chem. Soc. Chem. Commun.* 1974, 498.

(17) Cuthbertson, E.; MacNicol, D. D. *Tetrahedron Lett.* 1975, 1893.

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(21) Kawamura, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* 1977, 50, 2021.

(22) Uemura, S.; Wakasugi, M.; Okano, M. *J. Organomet. Chem.* 1980, 194, 277.

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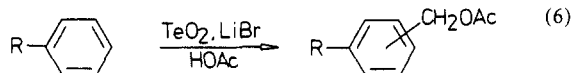
(24) Wenkert, E.; Leftin, M. H.; Michelotti, E. L. *J. Chem. Soc. Chem. Commun.* 1984, 617.

(25) Osuka, A.; Suzuki, H. *Tetrahedron Lett.* 1983, 24, 5109.

(26) Osuka, A.; Mori, Y.; Shimizu, H.; Suzuki, H. *Tetrahedron Lett.* 1983, 24, 2599.

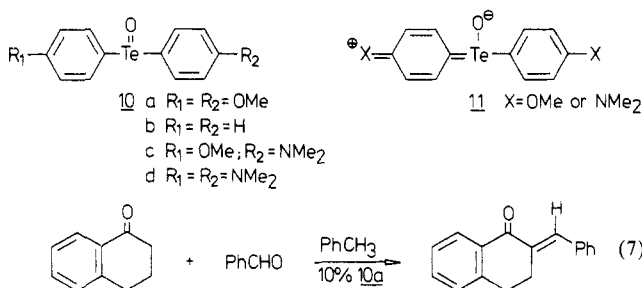
(27) Bergman, J.; Engman, L. *Tetrahedron Lett.* 1978, 3279.

6). The slow but clean reaction could only be per-



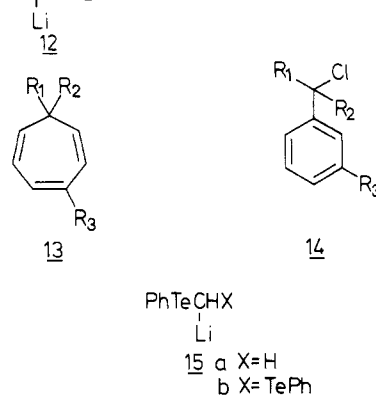
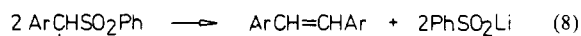
formed in acetic acid in the presence of a lithium halide (to solubilize the tellurium dioxide). Increasing alkyl substitution gave higher yields of acetoxymethylated compounds but concomitant formation of secondary products such as diarylmethane derivatives was also promoted. The acetoxymethyl group is of course derived in some way from the solvent acetic acid. A comprehensive product analysis suggested a carbene mechanism (involving acetoxycarbene,  $:\text{CHOAc}$ ) as being more probable than an electrophilic or radical one. One report in the patent literature describes the formation of phenylacetic acid from benzene using very similar reaction conditions to those giving acetoxymethylation.<sup>29</sup> This difference might possibly be attributed to the use of pressurized oxygen in the patent procedure.

Bis(*p*-methoxyphenyl) telluroxide (10a) has been found to function as a mild catalyst for a variety of aldol reactions.<sup>30,31</sup> The condensations were typically carried out in aprotic solvents like toluene or dimethyl sulfoxide by using 10 mol % of the catalyst (eq 7). The catalytic



activity of telluroxide 10a probably has to be attributed to the basic properties of the telluroxide oxygen. Cava<sup>31</sup> has shown that the efficacy of an aryl telluroxide as an aldol catalyst is highly dependent upon substituent effects. Diphenyl telluroxide (10b) was practically ineffective for the condensation of  $\alpha$ -tetralone with benzaldehyde whereas the dimethylamino-substituted derivatives 10c and 10d were even more active than compound 10a. This demonstrates the importance of the electron-donating resonance effect through the tellurium atom of the telluroxide (e.g., resonance form 11). The polarization of the oxygen-tellurium bond should certainly increase the basic properties of the telluroxide.

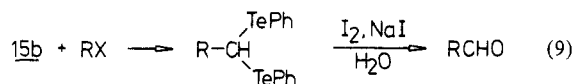
Another type of tellurium-catalyzed carbon-carbon bond-forming reaction is described in eq 8.  $\alpha$ -Lithiated benzylic sulfones 12 were found to slowly give *sym*-1,2-diarylethylenes when kept in tetrahydrofuran at ambient temperature for several days.<sup>32</sup> This long reaction time was drastically reduced if a small amount (20 mol %) of finely crushed elemental tellurium was added to the reaction. A significant change in the isomeric composition of the product stilbenes in the uncatalyzed (>97% *E*) vs. the tellurium-catalyzed



process (15–35% *Z* isomer) was a further indication that tellurium played an active part in the reaction. The definite form of this participation is as yet unclear but the initial step presumably involves insertion of tellurium into the carbon-lithium bond of the  $\alpha$ -lithiated sulfone 12.

In connection with the stilbene synthesis it was also discovered that tellurium tetrachloride was highly effective in promoting *Z*  $\rightarrow$  *E* isomerizations in 1,2-diarylethylenes. This is not surprising in view of the reported cationic oligomerizations and polymerizations of olefins and benzyl chlorides catalyzed by  $\text{TeCl}_4$ .<sup>33</sup> Cycloheptatrienes 13 were reported to undergo a rearrangement to benzyl chloride derivatives 14 under the influence of tellurium tetrachloride.<sup>34</sup>

Carbanions adjacent to di- or tetravalent tellurium are stabilized to a similar extent as those  $\alpha$  to sulfur and selenium. The synthetic possibilities of this observation have not yet been fully realized. Seebach and co-workers<sup>35</sup> prepared mono- and bis(phenyltelluro)methylolithium (15a and 15b) and studied their reactivity toward various electrophiles. Ogura has used compound 15a for olefin synthesis<sup>36</sup> and the homologation of alkyl halides<sup>37</sup> (vide infra) and demonstrated the synthetic equivalency of compound 15b to a formyl carbanion<sup>37</sup> (eq 9). Vinylic carbanions  $\alpha$  to tellurium



are also readily prepared as demonstrated by Kauffmann.<sup>38</sup>

### Functional Group Interconversions

The successful use of tellurium in organic synthesis does not only require its facile introduction into a variety of organic compounds. There must also be established some constructive ways to bring about the removal of tellurium from the organic moiety. Therefore considerable attention has been devoted to the conversion of the C-Te bond into a C-X bond (where X is hydrogen or another heteroatom). Other areas of current interest include oxidation and reduction reactions using tellurium in various oxidation states.

(33) Albeck, M.; Tamari, T. *J. Organomet. Chem.* 1982, 238, 357.

(34) Albeck, M.; Tamari, T.; Sprecher, M. *J. Org. Chem.* 1983, 48, 2276.

(35) Seebach, D.; Beck, A. K. *Chem. Ber.* 1975, 108, 314.

(36) Otsubo, T.; Ogura, F.; Yamaguchi, H.; Higuchi, H.; Sakata, Y.; Misumi, S. *Chem. Lett.* 1981, 447.

(37) Chikamatsu, K.; Otsubo, T.; Ogura, F.; Yamaguchi, H. *Chem. Lett.* 1982, 1081.

(38) Kauffmann, T.; Ahlers, H. *Chem. Ber.* 1983, 116, 1001.

(28) Bergman, J.; Engman, L. *J. Org. Chem.* 1982, 47, 5191.

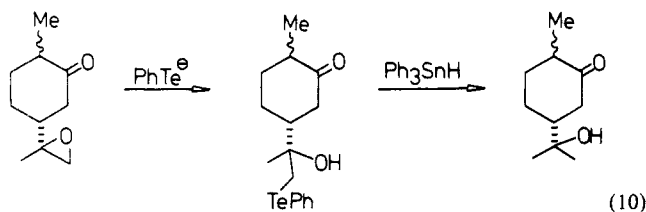
(29) U.S. Patent 4 237 314, 1980.

(30) Engman, L.; Cava, M. P. *Tetrahedron Lett.* 1981, 22, 5251.

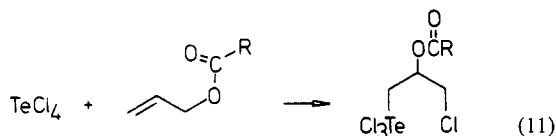
(31) Akiba, M.; Lakshminathan, M. V.; Jen, K.-Y.; Cava, M. P. *J. Org. Chem.* 1984, 49, 4819.

(32) Engman, L. *J. Org. Chem.* 1984, 49, 3559.

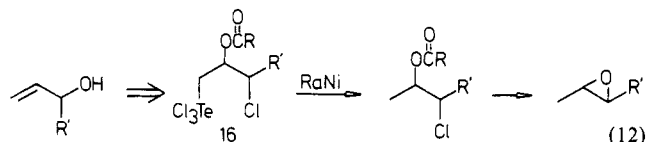
The transformation of a C-Te bond into a C-H bond can be conveniently performed by using a tin hydride ( $\text{Ph}_3\text{SnH}^{10}$  or  $\text{Bu}_3\text{SnH}^{39}$ ) or Raney nickel.<sup>40,41</sup> Equation 10 shows an example involving an overall reduction of an epoxide in the presence of a carbonyl group.<sup>10</sup>



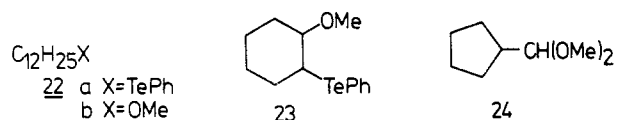
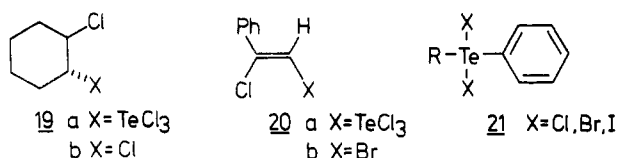
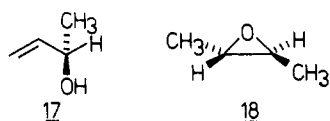
Tellurium tetrachloride undergoes a unique 1,3-addition reaction with allylic esters (eq 11). The elements



of Cl and  $\text{TeCl}_3$  are added in a 1,3-syn fashion to allow migration of the acyloxy group on the opposite side of the molecule. In combination with hydrotelluration (Raney nickel) and alkaline hydrolysis/ring closure of the resulting chlorohydrin ester, the whole reaction sequence is in principle equivalent to a direct ring closure of an allylic alcohol to an epoxide (eq 12).



When  $\alpha$ -substituents were introduced in the allylic ester, only the erythro from **16** of the chlorotelluration product was stereospecifically obtained. This complete control of the stereochemistry was taken advantage of in a conversion of (*S*)- $\alpha$ -methylallyl alcohol (**17**) into *trans*-(2*S*,3*S*)-2,3-epoxybutane (**18**).<sup>41</sup>



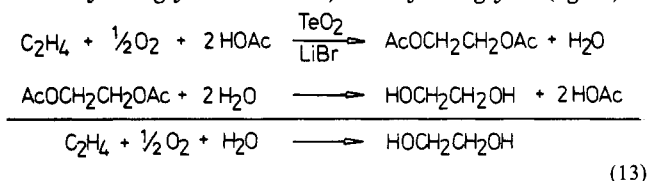
The replacement of tellurium by halogen may be achieved by the use of a heat-, light-, or oxidation-induced 1,2-tellurium halogen shift of organytellurium trihalides or diorganytellurium dihalides. Thus, compound **19a** afforded a 90% yield of 1,2-dichlorocyclohexane (**19b**) (*trans/cis* = 93/7) when heated in dioxane with *tert*-butyl hydroperoxide.<sup>42</sup> Aryl- or alkenyl-

bonded trichlorotelluro groups produced the corresponding chloro compounds with less success. Bromo- and iododetelluration could in these cases be induced by treatment with the respective halogen (e.g., **20a**  $\rightarrow$  **20b**).<sup>43</sup> Ogura found that 1,2-migration of halogen to an alkyl group R occurred readily when compounds **21** were heated in dimethylformamide at 100 °C for 1 h.<sup>37</sup>

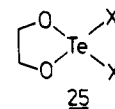
Uemura<sup>44</sup> has developed a method for the replacement of a phenyltelluro moiety by a methoxy group (**22a**  $\rightarrow$  **22b**). This reaction occurs at ambient temperature in methanol in the presence of excess *m*-chloroperbenzoic acid. Many substitutions were accompanied by rearrangement of the carbon skeleton (e.g., **23**  $\rightarrow$  **24**), thus indicating the involvement of carbonium ions as intermediates. A related 1,2-phenyl migration occurred in the crucial step of a new preparation of 2-arylpropanoic acids from  $\alpha$ -phenyltelluro-substituted acetophenones.<sup>45</sup>

The [2,3]-sigmatropic rearrangement of allylic tellurides represents a way of transforming a C-Te bond directly into a C-OH bond.<sup>46</sup> However, the instability of many allylic tellurium compounds will probably hinder future development of this strategy.

Catalytic systems containing tellurium dioxide have attracted considerable attention in recent years for the liquid-phase oxidation of olefins. The most notable development was made by Halcon, who attempted to commercialize a process for the oxidation of ethylene, via ethylene glycol diacetate, to ethylene glycol (eq 13).<sup>47</sup>



The mechanism of this reaction has become the topic of some speculation. One of the early patents suggested a cyclic intermediate, **25**, which would then undergo solvolysis to give the product. A detailed stereochemical



study<sup>48</sup> rejected this mechanism and favored an initial electrophilic attack (e.g., bromotelluration) by a solubilized tellurium(IV) species. The second step would require the conversion of the C-Te bond to a C-OAc bond and solvolysis of the resulting C-Br bond. Two recent patents<sup>49</sup> strongly support this mechanistic view in demonstrating 1,2-tellurium acetoxy shifts (eq 14). 1,3-Dienes afforded mixtures of diacetoxybutenes when oxidized with  $\text{TeO}_2$ .<sup>50</sup>

The synthesis of olefins by the syn elimination of a selenoxide has become one of the most widely employed

(43) Uemura, S.; Fukuzawa, S.; Wakasugi, M.; Okano, M. *J. Organomet. Chem.* **1981**, *214*, 319.

(44) Uemura, S.; Fukuzawa, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 471.

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(48) Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979**, *181*, 335.

(49) U.S. Patent 4 260 814, 1981; 4 271 090, 1981.

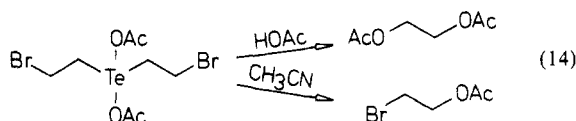
(50) Uemura, S.; Fukuzawa, S.; Patil, S. R.; Okano, M. *J. Chem. Soc. Perkin Trans. 1* **1985**, 499.

(39) Comasseto, J. V.; Petragani, N. *Synth. Commun.* **1983**, *13*, 889.

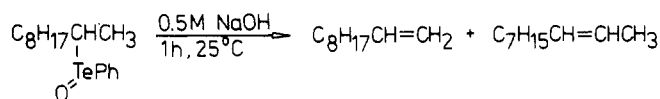
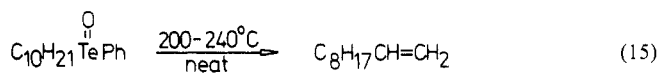
(40) Bergman, J.; Engman, L. *J. Am. Chem. Soc.* **1981**, *103*, 5196.

(41) Engman, L. *J. Am. Chem. Soc.* **1984**, *106*, 3977.

(42) Uemura, S.; Fukuzawa, S. *J. Organomet. Chem.* **1984**, *268*, 223.

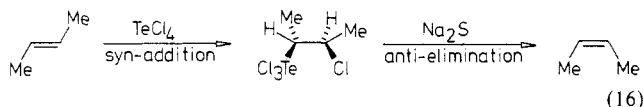


modern synthetic reactions. In contrast, the telluroxide elimination reaction initially appeared less promising due to low yields, contamination by oxygenated products, and high reaction temperatures.<sup>51</sup> However, the synthetic potential of the reaction was considerably increased when Uemura discovered that *sec*-alkyl phenyl telluroxides were decomposed much more readily to olefins than *n*-alkyl phenyl telluroxides<sup>52</sup> (eq 15). If tellurium was oxidized by chloramine-*T* (*N*-



chloro-*N*-sodio-4-methylbenzenesulfonamide) also, *n*-alkyl groups bonded to a TePh moiety were eliminated as olefins in high yields.<sup>36</sup> This whole area has much potential for future development.

Tellurium methodology has provided a new procedure for the mild inversion of olefins. This method is based on a unique syn addition/anti elimination reaction of tellurium tetrachloride.<sup>53</sup> In the presence of a radical inhibitor the competing nonspecific radical mechanism can be suppressed in favor of a stereospecific syn addition (eq 16). The anti elimination was



induced by aqueous Na<sub>2</sub>S. Future studies will hopefully serve to define the compatibility of the rather aggressive TeCl<sub>4</sub> with other functional groups.

A series of closely related, easily prepared tellurium reagents have recently been introduced as new selective reducing agents in organic chemistry. Table I summarizes some mild reductive transformations brought about by sodium hydrogen telluride, NaHTe. Isolated double bonds as well as carbonyl groups are not affected by the reagent whereas conjugated double bonds are hydrogenated. Hydrogen telluride, H<sub>2</sub>Te<sup>62</sup> and arene

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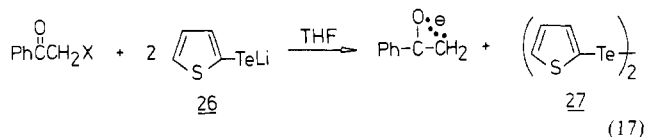
(b) Suzuki, H.; Takaoka, K. *Chem. Lett.* **1984**, 1733.

Table I  
Synthetic Transformations Using  
Sodium Hydrogen Telluride, NaHTe

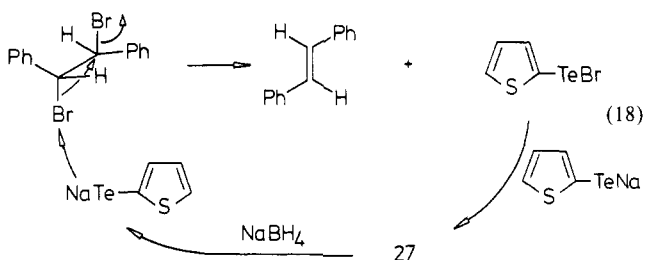
substrate	product	ref
	ROCH <sub>2</sub> Ph	54
		55
PhCH=CH-CHO	PhCH <sub>2</sub> CH <sub>2</sub> CHO	56
		57
	PhCH=CH-CHO	58
PhNO <sub>2</sub>	PhNH <sub>2</sub>	59
		60
		61a
PhN <sub>3</sub>	PhNH <sub>2</sub>	61b

tellurols, ArTeH,<sup>63</sup> have also shown reducing properties of some value. In contrast to NaHTe all these reagents reduce aromatic aldehydes to benzyl alcohols.

Lithium 2-thiophenellurolate (**26**) reductively removes a variety of electronegative  $\sigma$ -substituents (Cl, Br, I, OAc, MeSO<sub>3</sub>, SPh) from ketones and acids.<sup>64</sup> The reduced carbonyl compound is obtained as an enolate together with bis(2-thienyl)ditelluride (**27**) (eq 17). In



contrast to the other tellurium-based reducing agents, the tellurolate system can easily be turned into a catalytic one if sodium borohydride is used as the stoichiometric reducing agent. This catalytic procedure has been demonstrated for the debromination of *vic*-dibromides to olefins<sup>65</sup> (eq 18). Not only does the di-



telluride function as a source of tellurolate ions, but also it serves as an indicator changing color from deep red to colorless when all the substrate is consumed. A series

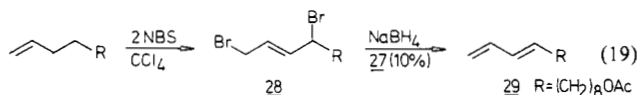
(62) Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1009. Kambe, N.; Kondo, K.; Sonoda, N. *Ibid.* **1980**, *19*, 1009.

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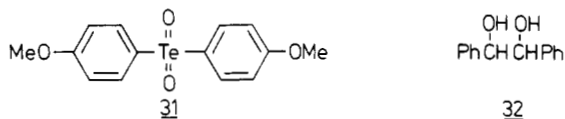
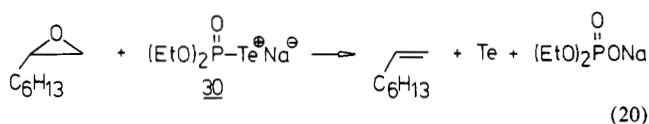
(64) Engman, L.; Cava, M. P. *J. Org. Chem.* **1982**, *47*, 3946.

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of 2,4-dibromo-2-enes (**28**) were catalytically 1,4-debrominated to give 1,3-dienes ( $E/Z \approx 9/1$ ) under very mild reaction conditions.<sup>66</sup> The required 1,4-bromo-2-enes were obtained by treating terminal olefins with two equivalents of NBS (allylic rearrangement). A two-step synthesis of the red bollworm moth sex pheromone (**29**) demonstrates the synthetic potential of the reaction (eq 19).



Sodium *O,O*-diethyl phosphotelluroate (**30**) represents another class of easily prepared reagents containing nucleophilic tellurium. In addition to its dehalogenating effect on  $\alpha$ -halo ketones,<sup>67</sup> compound **30** was found to smoothly deoxygenate epoxides to olefins<sup>68</sup> (eq 20).



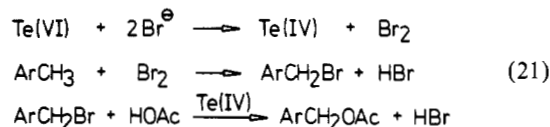
Te(IV) and Te(VI) compounds have also shown potential as oxidizing agents in organic synthesis. The easily available bis(*p*-methoxyphenyl)telluroxide (**10a**) has been used to mildly and selectively regenerate carbonyl compounds from their thiocarbonyl analogues in the presence of many other sensitive groups.<sup>69</sup>

The oxidizing properties of tellurium dioxide were tentatively explored in the 1940s. However, the low solubility in organic solvents restricted its use for many years. Finally it was found that TeO<sub>2</sub> could be dissolved in acetic acid containing a lithium halide. The application of this oxidation system for olefin oxidation and acetoxymethylation of aromatics has already been touched upon (vide supra). In addition, it might also be used for the regeneration of ketones from their corresponding semicarbazones, azines, and hydrazones.<sup>70</sup> Phenylhydrazines were oxidized to aryldiazonium halides whereas ketones underwent  $\alpha$ -acetoxylation.<sup>28</sup>

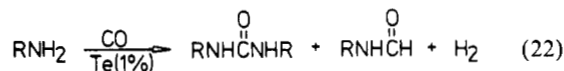
As expected, tellurium(VI) compounds show more potent oxidizing properties than their tellurium(IV) counterparts. Bis(*p*-methoxyphenyl) tellurone (**31**), the first definitely characterized tellurone,<sup>71</sup> was capable of oxidizing benzylic alcohols to benzaldehydes in refluxing

toluene. Vicinal diols were oxidatively cleaved as exemplified by the conversion of hydrobenzoin (**32**) to benzaldehyde.

Tellurium trioxide, TeO<sub>3</sub>, and its less expensive trihydrate, Te(OH)<sub>6</sub>, also function as oxidizing agents in acetic acid containing lithium bromide.<sup>28</sup> In contrast to TeO<sub>2</sub>, the Te(VI) compounds slowly oxidize bromide ions to Br<sub>2</sub> at elevated temperature. Alkyl aromatic compounds were readily side chain brominated by the action of this oxidizing system. Furthermore, the Te(IV) compound formed in the oxidation of bromide ion considerably promoted the solvolysis of the benzylic bromides to benzylic acetates (eq 21). It thus acts as an efficient recipient of HBr.



Elemental tellurium might also act as an oxidant as shown by Sonoda<sup>72</sup> in a unique catalytic process for carbonylation of amines to urea derivatives and formamides (eq 22). The oxidation state of tellurium is



probably oscillating between zero and -II (unstable H<sub>2</sub>Te → H<sub>2</sub> + Te) to close the catalytic cycle.

## Summary and Outlook

In this Account, we have described a number of synthetically useful transformations involving tellurium either in the form of a readily available starting material or as an easily prepared reagent. The former applications demonstrate the possibilities, after proper manipulations, to replace tellurium by other functional groups, including carbon. The tellurium reagents have found their applications primarily in the fields of oxidation and reduction reactions. Some of the tellurium-mediated transformations described in this article might be equally or even better performed by classical methodology. Others are entirely unique for tellurium and cannot be executed by other means. If organic tellurium chemistry is ever going to be included in the organic chemists standard arsenal of reagents and reactions, more unique transformations have to be developed. It should be clear from this paper that this process is on-going and rapidly progressing.

*It is a pleasure to acknowledge the significant contributions of my co-workers, whose names occur in the references. Financial support by the Swedish Natural Science Research Council is also gratefully acknowledged.*

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