In summary, our studied selenonium and telluronium cations obey most of the already established trends of chemical shifts and coupling constants in neutral organic selenium and tellurium compounds. Our multinuclear NMR data have allowed for the first time such comparisons to be made.

Experimental Section

Me_2Se and Me_2Te were purchased from Alfa and used without further purification. MeOTf and EtOTf were obtained from Aldrich and distilled once under dry nitrogen prior to use.

$Me_3Se^+{}^-OTf$, $Et_2MeSe^+{}^-OTf$, and $Me_3Te^+{}^-OTf$ were prepared by methylation of the corresponding dialkyl precursors with 1 mol equiv of methyl triflate (0 °C–room temperature) in Freon-113 solvent under dry nitrogen, by the same procedure described by Olah et al.[11] for the preparation of the fluorosulfates. $Et_3Se^+{}^-OTf$ and $Me_2EtTe^+{}^-OTf$ were similarly prepared by ethylation with EtOTf. The cation salts were isolated as stable solids and were found to be indefinitely stable when refrigerated under nitrogen. Triflic acid solutions of the cation salts were also indefinitely stable when stored under nitrogen.

Protonation in Superacids and Donor–Acceptor Complex Formation in SbF_5. (a) Protonation with Magic Acid. Typically a ^{13}C NMR tube was charged with ca. 1.5 mL of magic acid under nitrogen and diluted with 1.5 mL of SO_2 (vortex). The solution was then carefully added to the dialkyl selenide or telluride precursor (100 mg), placed in a ^{13}C NMR tube, and diluted with ca. 0.5 mL of SO_2, at −70 °C with efficient vortex mixing to avoid overheating. Dilution of Me_2Se with SO_2 is rather exothermic. The addition of SO_2 to Et_2Se is less exothermic, but a pale yellow color develops.

(b) Protonation of Me_2Te with HF/BF_3. Following a similar procedure as that reported by Olah et al.,[11] in a 10-mm quartz NMR tube cooled to −70 °C was placed 2 mL of HF. Precooled Me_2Te (ca. 100 mg) was slowly added (vortex). The resulting solution was then saturated with BF_3.

The donor–acceptor complexes were prepared as follows: The dialkyl selenide precursor (ca. 100 mg) cooled to −70 °C was carefully diluted with ca. 1 mL of SO_2ClF (vortex). A colorless, homogeneous solution of SbF_5 (2–3-fold excess over the precursor) dissolved in SO_2ClF (1 mL) was then carefully added to the substrate in SO_2ClF with vortex mixing while at dry ice–acetone temperature.

Attempted Preparation of $Me_2Te^{\delta+}\rightarrow{}^{\delta-}SbF_5$. Addition of SO_2ClF (1 mL) to Me_2Te (150 mg) cooled to −70 °C was extremely exothermic, and a red color developed. Slow addition of SbF_5 in SO_2ClF resulted in a *violent* reaction forming a viscous gum (Polytelluride).

NMR Measurements. All spectra were recorded on a Varian FT.80 instrument. The ^{77}Se and ^{125}Te spectra were run with a broad-band probe using the external (built-in) deuterium lock. The chemical shifts were referenced to neat (external) Me_2Se and Me_2Te, respectively. Whereas some of the ^{13}C spectra were recorded with the broad-band probe, the majority were run with the switchable carbon–proton probe with an external (5-mm) capillary of acetone-d_6, placed inside the 10-mm sample tubes and used as lock and reference. ^{77}Se–^{13}C and ^{125}Te–^{13}C coupling constants were measured from the ^{77}Se and ^{125}Te satellites in the ^{13}C proton-decoupled spectra.

Acknowledgment. We thank Kent State University for research support.

Registry No. $^{13}Me_3{}^{77}Se^+{}^-OTf$, 109528-06-5; $^{13}Me_2{}^{13}Et{}^{77}Se^+{}^-OTf$, 109528-08-7; $^{13}Et_2{}^{13}Me{}^{77}Se^+{}^-OTf$, 109528-10-1; $^{13}Et_3{}^{77}Se^+{}^-OTf$, 109528-12-3; $^{13}Me_2H{}^{77}Se^+{}^-[FSO_3(SbF_5)]$, 109528-20-3; $^{13}Me_2{}^{77}Se^{\delta+}{}^{\delta-}SbF_5$, 109528-21-4; $^{13}Et_2H{}^{77}Se^+{}^-[FSO_3(SbF_5)]$, 109528-23-6; $^{13}Et_2{}^{77}Se^{\delta+}{}^{\delta-}SbF_5$, 109528-24-7; $^{13}Me_2{}^{13}Et{}^{125}Te^+{}^-OTf$, 109528-14-5; $^{13}Me_2H{}^{125}Te^+{}^-BF_4$, 109528-16-7; $^{13}Me_3{}^{125}Te^+{}^-OTf$, 109528-18-9; ^{77}Se, 14681-72-2; ^{125}Te, 14390-73-9.

Communications

Synthesis of 4-Hetero-Substituted Pyranosides via Dioxenium Cation–Olefin Cyclization

Summary: Ortho esters and homoallylic alcohols in the presence of Lewis acids stereoselectively provide 4-hetero-substituted pyranosides in the first examples of dioxenium cation cyclization onto unactivated olefins.

Sir: Carbocation–olefin cyclization continues to be a powerful method of constructing carbocyclic and heterocyclic ring systems.[1] The utility of the method lies in its ability to simultaneously form carbon–carbon bonds and introduce heterofunctionality in a predictable and stereocontrolled manner. A variety of heteroatom-stabilized carbocations have been cyclized including oxenium,[2] thienium,[3] dithienium,[4] and iminium[5] carbocations. We report the cyclization of dioxenium cations[6] onto unactivated olefins resulting in the formation of 4-hetero-substituted pyranosides. Pyranosides hydroxylated at the 4-position are key substructures in a number of naturally occurring substances such as the avermectins,[7] aplysiatoxin–oscillatoxins,[8] latrunculins,[9] talaromycins,[10] and acutiphycin,[11] among others.

When a dichloromethane solution of an ortho ester was treated with 0.5–2 equiv of a Lewis acid rapid formation of a dioxenium cation salt ensued, usually evidenced as a white precipitate. Addition of a homoallylic alcohol re-

(1) Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapters 5 and 6.
(2) (a) Winstead, R. C.; Simpson, T. H.; Lock, G. A.; Schiavelli, M. D.; Thompson, D. W. *J. Org. Chem.* **1986**, *51*, 275. (b) Johnson, W. S.; Chen, Y.-G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 6653. (c) Overman, L. E.; Blumenkopf, T. A. *Chem. Rev.* **1986**, *86*, 857. Also see: Nussbaumer, C.; Frater, G. *Helv. Chim. Acta* **1987**, *70*, 396.
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(5) Schoemaker, H. E.; Dijkink, J.; Speckamp, W. N. *Tetrahedron* **1978**, *34*, 163.
(6) To our knowledge, only one previous example of this process has been described, in which the cyclization occurred onto an enol ether. See: Kocienski, P.; Street, S. D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 571.
(7) Albers-Schonberg, G.; Arison, B. H.; Chabala, J. C.; Douglas, A. W.; Eskola, P.; Fisher, M. H.; Lusi, A.; Mrozik, H.; Smith, J. L.; Tolman, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4216.
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(9) Spector, I.; Shochet, N. R.; Kashman, Y.; Groweiss, A. *Science (Washington, D.C.)* **1983**, *219*, 493.
(10) Lynn, D. G.; Phillips, N. J.; Hutton, W. C.; Shabanowitz, J.; Fennell, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 7319.
(11) Barchi, J. J.; Moore, R. E.; Patterson, G. L. M. *J. Am. Chem. Soc.* **1984**, *106*, 8193.

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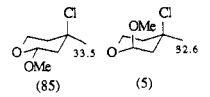
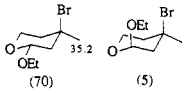
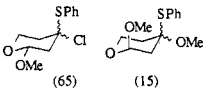
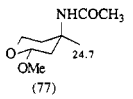
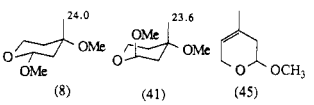
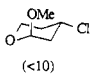
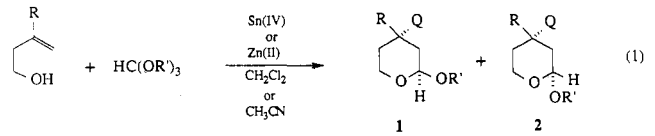
Table I. Results of Dioxenium Cation-Olefin Cyclizations

olefinic alcohol	ortho ester	conditions[a]	product(s)[b,c]
	$HC(OCH_3)_3$	1.1 equiv.$SnCl_4$ CH_2Cl_2 / -78°C, 2 h	 (85) (5)
	$HC(OEt)_3$	0.5 equiv.$SnBr_4$ CH_2Cl_2 / -20°C, 4 h	 (70) (5)
	$HC(OCH_3)_3$	1.6 equiv.$SnCl_4$ CH_2Cl_2 / -20°C, 1.5 h	 (65) (15)
	$HC(OCH_3)_3$	1.1 equiv. $SnCl_4$ CH_3CN / -20°C, 2 h	 (77)
	$HC(OCH_3)_3$	2.0 equiv. $ZnBr_2$ CH_2Cl_2 / 25°C, 10 h	 (8) (41) (45)
	$HC(OCH_3)_3$	1.1 equiv. $SnCl_4$ CH_2Cl_2 / 0°C, 2 h	 (<10)

[a] All reactions were run under an atmosphere of dry nitrogen; workup involved quenching with aqeuous $NaHCO_3$ solution and dichloromethane extraction. [b] Yields (in parentheses) refer to products isolated by HPLC on silica gel. [c] ^{13}C NMR chemical shifts (ppm, δ, $CDCl_3$) of quaternary methyl groups are shown on structures.

sulted in the formation of 4-hetero-substituted pyranosides (**1** and **2**) at temperatures as low as −78 °C (eq 1). The



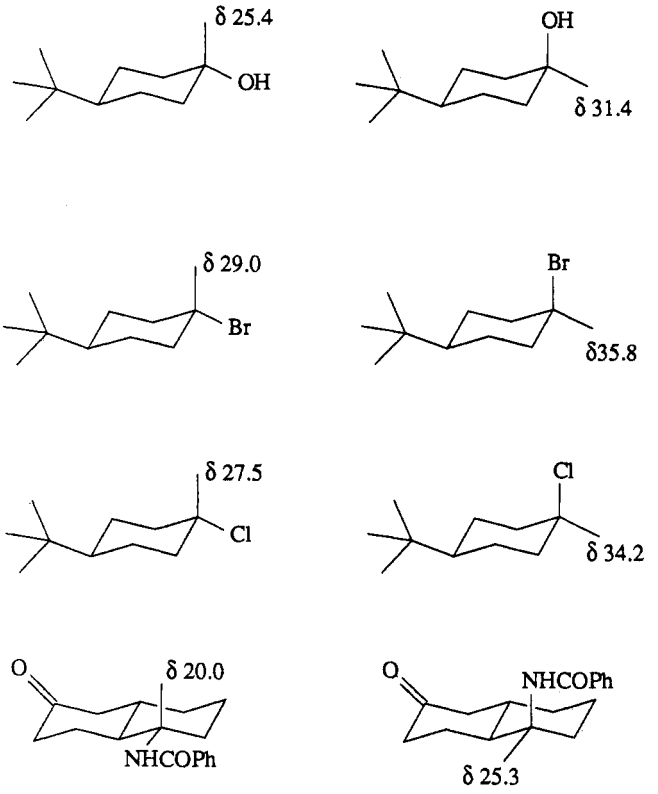
(1)

results are shown in Table I. Note that a number of heteroatomic groups can be incorporated at the 4-position depending on the solvent and Lewis acid chosen. Tin(IV) salts appear to be the Lewis acids of choice, allowing termination of cyclization by a number of different groups; $TiCl_4$ gave erratic results despite its success in oxenium cation cyclizations.[2] In contrast, Zn(II) salts showed little tendency toward incorporation of the counterion in the product, allowing other pathways for termination of the cyclization, including elimination.

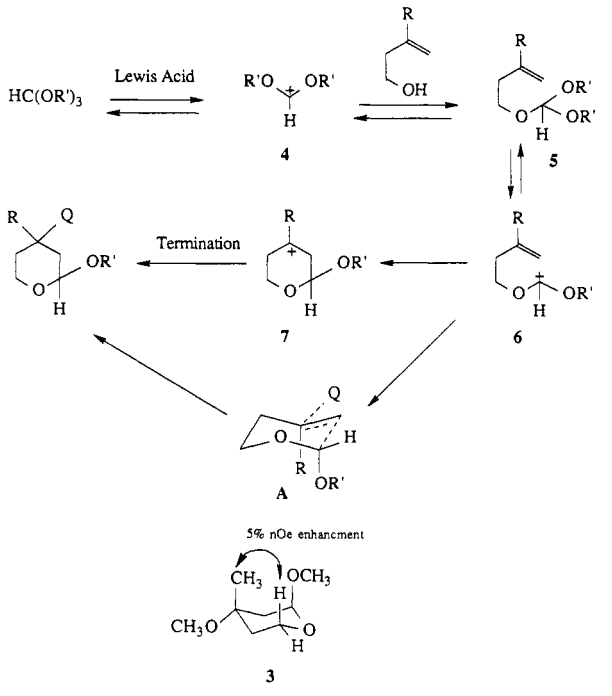
A predominance of one isomer was generally observed in the reactions with Sn(IV). In each case, the major isomer was identified as **1** (Q = Cl, Br, NHAc, OR). These assignments were based on the coupling constants of the acetal protons and the ^{13}C NMR shifts of the quaternary methyl groups, with the assumption that the compounds prefer chair-like conformations. For example, in the first entry of the table the major product isolated possessed an axial acetal hydrogen ($J \sim 3$ and 9 Hz) and an equatorial methyl group indicated by a low field ^{13}C methyl absorption, consistent with conformationally locked model compounds such as those shown in Scheme I.[12] Additionally, it seemed odd to us that the bismethoxy pyranosides isolated in the reaction with $ZnBr_2$ (Table I, fifth entry) would possess axial methyl groups. However, this assignment was

(12) Crews, P.; Naylor, S.; Hanke, F. J.; Hogue, E. R.; Kho, E.; Braslau, R. *J. Org. Chem.* **1984**, *49*, 1371. Stevens, R. V.; Albizati, K. F. *J. Org. Chem.* **1985**, *50*, 632.

Scheme I



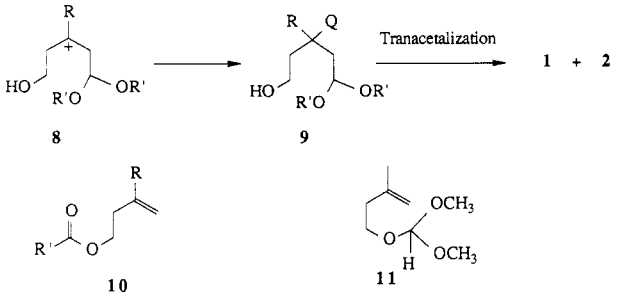
Scheme II



supported by the observation of a 1,3-diaxial NOE enhancement of ca. 5% between the quaternary methyl group and the axial hydrogen in the 6-position in **3**.

We tentatively postulate the mechanism shown in Scheme II for this process. Combination of the Lewis acid with the ortho ester results in reversible formation of the dioxenium cation **4**. Cation **4** combines with the homoallylic alcohol to give the mixed ortho ester **5** which is presumably in equilibrium with a second dioxenium cation **6**. In the Zn(II) examples, the lack of stereochemical control and the production of elimination products suggest the formation of a full carbocation **7**. This is supported

Scheme III



by control experiments in which the bismethoxy pyranosides (3 and its diastereomer) were individually resubjected to the reaction conditions; no isomerization or elimination of the tertiary ethers was observed.[13]

To rationalize the predominant product of one isomer when Sn(IV) is used and the absence of elimination products, we suggest that these cyclizations are preferentially occurring via the transition state A in which the dioxenium cation and the terminating group approach the olefin in a trans antiperiplanar fashion and in which the alkoxy group has adopted an axial orientation, thus maximizing any benefit derived from an "anomeric effect".[14] This mechanism presupposes that the reaction products are produced kinetically. When pure **1** or **2** (Q = Cl; R, R′ = CH_3) were resubjected to the reaction conditions, no equilibration to the opposite diastereomer occurred, supporting the idea that the reaction is kinetically controlled.

An alternate mechanism involving initial "Prins-like" addition of the dioxenium cation to the olefin to give 8 followed by transacetalization is possible (Scheme III). We have never detected intermediates such as **9**. However, in certain cases we have isolated esters of general structure **10**, presumably arising by hydration of the intermediate cation 6 upon workup. In addition, we have synthesized the presumed intermediate mixed ortho ester **11**[15] and found that cyclization to **1** (Q = Cl; R,R′ = CH_3) occurs when **11** is treated with $SnCl_4/CHCl_2$ at −20 °C. These data support the mechanism shown in Scheme II.

This methodology opens up possibilities for the construction of a variety of oxygenated heterocycles. Further investigation of this process and its application to natural product synthesis are currently in progress.

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Registry No. 1 (R = R^1 = Me, Q = Cl), 109553-12-0; 1 (R = Me, R^1 = Et, Q = Br), 109553-13-1; 1 (R = R^1 = Me, Q = NHAc), 109553-14-2; 1 (R = OMe, R^1 = Q = Me), 109553-15-3; 1 (R = H, R^1 = Me, Q = Cl), 6559-36-0; 2 (R = R^1 = Me, Q = Cl), 109553-16-4; 2 (R = Me, R^1 = Et, Q = Br), 109553-17-5; 2 (R = OMe, R^1 = Q = Me), 109553-18-6; 11, 109553-19-7; CH_2=C(Me)$(CH_2)_2$OH, 763-32-6; CH_2=C(SPh)$(CH_2)_2$OH, 109553-20-0; CH_2=CH$(CH_2)_2$OH, 627-27-0; $CH(OMe)_3$, 149-73-5; $CH(OEt)_3$, 122-51-0; $^+CH(OMe)_2$, 23012-07-9; $^+CH(OEt)_2$, 44612-00-2; $SnCl_4$, 7646-78-8; $SnBr_4$, 7789-67-5; $ZnBr_2$, 7699-45-8; 4-chloro-2-methoxy-4-(phenylthio)tetrahydropyran, 109553-21-1; 2,4-dimethoxy-4-(phenylthio)tetrahydropyran, 109553-22-2; 3,6-dihydro-2 methoxy-4-methyl-2*H*-pyran, 31080-83-8.

(13) We are grateful to a referee for suggesting these experiments.
(14) Although generally considered a ground-state phenomenon, the anomeric effect might be manifested in a reaction involving a late transition state (in this case a kinetic effect), such as one involving a highly stabilized cation. Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1983.
(15) We have found that these mixed ortho esters can be synthesized in high yields by treating an alcohol in CH_2Cl_2 with an excess of trimethyl orthoformate using $MgCl_2$ to facilitate the exchange. These results will be described elsewhere.

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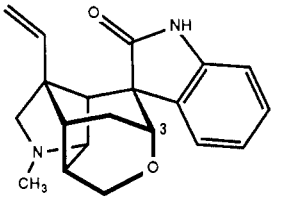
Intramolecular Alkene Arylations for Rapid Assembly of Polycyclic Systems Containing Quaternary Centers. A New Synthesis of Spirooxindoles and Other Fused and Bridged Ring Systems

Summary: The preparation of a variety of tricyclic ring systems by palladium-catalyzed cyclizations of unsaturated aryl halides is described. These examples demonstrate (a) the ease with which quaternary centers can be formed by intramolecular Heck arylations, (b) that intramolecularity can overcome the usual reluctance of highly substituted alkenes to participate in palladium-catalyzed reactions, and (c) that the addition of silver salts dramatically reduces double-bond isomerizations of the cyclization products.

Sir: The palladium-catalyzed arylation of alkenes (Heck arylation) is a powerful method for the preparation of functionalized aromatics.[2] Intramolecular versions of this reaction have received some attention,[2] particularly in the area of heterocyclic synthesis,[3] since the pioneering early investigations by the Ban[4] and Heck[5] groups. As part of our ongoing studies pertaining to the total synthesis of the complex hexacyclic alkaloid gelsemine (1),[6] we recently



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examined the use of intramolecular Heck arylations for the synthesis of 3-spiro-2-oxindoles.[7] These investigations have demonstrated the power of this reaction to solve formidable synthetic problems such as the elaboration of quaternary carbon centers, aspects of this chemistry not

(1) NIH NRSA Postdoctoral Fellow (GM-11332), 1986-1987.
(2) Heck, R. F. *Org. React. (N.Y.)* **1982**, *27*, 345.
(3) Recent publications, not reviewed in ref 2, include: (a) Odle, R.; Blevins, B.; Ratcliff, M.; Hegedus, L. S. *J. Org. Chem.* **1980**, *45*, 2709. (b) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Org. Chem.* **1980**, *45*, 2938. (c) Kasahara, A.; Izumi, T.; Murakami, S.; Yanai, H.; Takatori, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 927. (d) Negishi, E.-I.; Tour, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 8289.
(4) Mori, M.; Chiba, K.; Ban, Y. *Tetrahedron Lett.* **1977**, 1037.
(5) Terpko, M. O.; Heck, R. F. *J. Am. Chem. Soc.* **1979**, *101*, 5281.
(6) (a) Oh, T.; Overman, L. E. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO, April, 1987; American Chemical Society: Washington, DC; Abstract ORGN 135. (b) See also; Joule, J. A. In *Indoles Part Four. The Monoterpene Indole Alkaloids*; Saxton, J. E., Ed.; John Wiley: New York, 1983; Chapter 5, pp 239-243.
(7) For a recent report of the synthesis of saturated 3-spiro-2-oxindoles by radical cyclization, see: Jones, K.; Thompson, M.; Wright, C. *J. Chem. Soc., Chem. Commun.* **1986**, 115. Leading citations to other syntheses of 3-spiro-2-oxindoles can be found in ref 3 of this paper.

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