sonicated in the presence of 1.010 g (10 mmol) of diisopropylamine. After disappearance of the metal (usually 15–30 min), and standardization, the solution can be used for deprotonations as usual.

The same experiment effected in the presence of 0.440 g (5 mmol) of 2-methylpropanoic acid gave a thick white precipitate after 5 min, which progressively redissolve to give a slightly turbid solution. Quenching with 0.53 g (5 mmol) of benzaldehyde and stirring for 1 h at 20 °C gave a slightly yellow solution which was hydrolyzed (20 mL of water) and extracted with ether. The alkaline phase was acidified (aqueous 2 N HCl) and extracted with ether, and the organic extract was washed (2 × 20 mL water), dried (Na_2SO_4), and evaporated. The residue was recrystallized (hexane/AcOEt) to give 0.757 g (78% yield) of **2,2-dimethyl-3-hydroxy-3-phenylpropanoic acid:**[6] mp 132–133 °C (lit.[6] mp 133–134 °C); IR 3400, 1700 cm^{-1}; NMR ($CDCl_3$) 1.28 (s, 6 H), 5.07 (s, 1 H), 6.50–7.00 (m, 2 H, exchangeable in D_2O), 7.45 (s, 5 H) ppm.

Large-Scale Preparation of LDA. *n*-Butyl chloride (46.3 g, 0.5 mol) and 50.6 g (0.5 mol) of diisopropylamine in 250 mL of dry THF in a round-bottom flask were placed in the sonicator. Lithium wire (7 g, 1 mol) was added in pieces of ca. 1 g each, progressively to avoid excessive heating. After 2 h of sonication, the metallic pieces were completely consumed and the yellow mixture containing precipitated LiCl was standardized (calculated yield, 91%).

General Procedure for Other Cases. The corresponding butyl chloride (93 mg, 1 mmol), lithium (14 mg, 2 mmol), and 1 mmol of the substrate in 2 mL of THF (THP in the case of the lithiation of anisole) were sonicated until no metal was left. Addition of the quenching agent (1 equiv) and reaction under stirring was followed by workup, after a TLC analysis had shown completion. Purification (chromatography) of the products gave samples that exhibited physical and spectral properties consistent with structures and literature data.

2-Furylphenylcarbinol:[7] liquid; IR 3375, 1500, 1450, 1015 cm^{-1}; NMR ($CDCl_3$) 2.60 (br s, 1 H, exchangeable in D_2O), 5.7–5.85 (m, 1 H), 6.05–6.15 (m, 1 H), 6.25–6.37 (m, 1 H), 7.25–7.50 (m, 6 H) ppm.

2-(1,3-Dithianyl)phenylcarbinol:[8] mp 73–74 °C (lit.[8] mp 71–72 °C); IR 3450, 2900, 1495, 1420, 1280 cm^{-1}; NMR ($CDCl_3$) 1.80–2.20 (m, 2 H), 2.50–3.15 (m, 5 H), 4.15 (d, J = 9 Hz, 1 H), 4.92 (d, J = 9 Hz, 1 H), 7.25–7.50 (m, 5 H) ppm.

Non-2-yn-1-ol:[9] liquid; IR 3325, 2925, 2275, 2225, 1430, 1140, 1010 cm^{-1}; NMR ($CDCl_3$) 0.75–1.10 (m, 3 H), 1.10–1.70 (m, 8 H), 1.80–2.08 (m, 1 H, exchangeable in D_2O), 2.08–2.35 (m, 2 H), 4.15–4.35 (m, 2 H) ppm.

1-Phenylpent-2-yn-1-ol:[10] liquid; IR 3350, 2980, 2280, 2230, 1460, 1010 cm^{-1}; NMR ($CDCl_3$) 1.17 (t, J = 9 Hz, 3 H), 2.15–2.45 (m, 3 H), 5.35–5.55 (m, 1 H), 7.30–7.70 (m, 5 H) ppm.

2-Phenyl-2-oxoethyl methyl sulfone:[11] mp 105–106 °C (lit.[11] mp 106–107 °C); IR 1680, 1310, 1160 cm^{-1}; NMR ($CDCl_3$) 3.15 (s, 3 H), 4.60 (s, 2 H), 7.39–7.70 (m, 3 H), 7.91–8.09 (m, 2 H) ppm.

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Registry No. LDA, 4111-54-0; BuLi, 109-72-8; *n*-BuCl, 109-69-3; *sec*-BuCl, 78-86-4; *t*-BuCl, 507-20-0; $(i\text{-Pr})_2NH$, 108-18-9; Li, 7439-93-2; $i\text{-PrCO}_2H$, 79-31-2; PhCHO, 100-52-7; $PhCH(OH)C(CH_3)_2CO_2H$, 23985-59-3; $PhOCH_3$, 100-66-3; CH_3I, 74-88-4; $2\text{-}H_3CC_6H_4OCH_3$, 578-58-5; $Ph_3P^+CH_2CH_3Br^-$, 1530-32-1; $Ph_2C{=}O$, 119-61-9; $Ph_2C{=}CHCH_3$, 778-66-5; $C_6H_{13}C{\equiv}CH$, 629-05-0; $(CH_2O)_n$, 30525-89-4; $PhCH(OH)C{\equiv}CCH_2CH_3$, 51207-10-4; $CH_3SO_2CH_3$, 67-71-0; $C_2H_5C{\equiv}CH$, 107-00-6; $C_6H_{13}C{\equiv}CCH_2OH$, 5921-73-3; $PhCO_2CH_3$, 93-58-3; $PhCOCH_2SO_2CH_3$, 3708-04-1; CH_3SOCH_3, 67-68-5; 2,2,6,6-tetramethylpiperidine, 768-66-1; lithium 2,2,6,6-tetramethylpiperidine, 38227-87-1; furan, 110-00-9; α-phenyl-furanmethanol, 4484-57-5; 1,3-dithiane, 505-23-7; α-phenyl-1,3-dithianemethanol, 5849-19-4.

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Selenium-77, Tellurium-125, and Carbon-13 NMR Chemical Shifts and One-Bond $^{77}Se-^{13}C$, $^{125}Te-^{13}C$, and $^{13}C-^{1}H$ Coupling Constants of Trialkylselenonium and Telluronium Triflates, Protonated Dialkylselenonium and Telluronium Cations, and Their Corresponding Donor–Acceptor Complexes

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There is substantial current interest in ^{77}Se and ^{125}Te NMR.[1-8] Pioneering work by McFarlane et al.[9,10] helped establish both selenium and tellurium chemical shifts as useful diagnostic tools. Most of the early measurements of chemical shifts and coupling constants were done by heteronuclear double-resonance technique in the proton NMR spectra. McFarlane et al.[9] were first to show the parallelism in chemical shifts between organoselenium and organotellurium compounds of similar structure, with ^{125}Te being slightly more sensitive (^{125}Te vs. ^{77}Se straight-line plot; slope 1.8).

In analogy with other heavy atoms, ^{77}Se and ^{125}Te chemical shifts are influenced by both paramagnetic (δ^p) and diamagnetic (δ^d) shielding contributions. The δ^d, which involves the inner electrons, is thought to be small and rather insensitive to changes in bonding. Moreover, both ^{77}Se and ^{125}Te chemical shifts are reported to be relatively insensitive to solvent effects.[9,10]

Whereas the literature on ^{77}Se and ^{125}Te chemical shifts of neutral substrates has been growing steadily over the past decade,[1-8] multinuclear NMR studies involving electron-deficient organic selenonium and telluronium cations

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Table I. Selenium-77 and Carbon-13 NMR Chemical Shifts and One-Bond $^{77}Se-^{13}C$ and $^{13}C-^{1}H$ Spin-Spin Coupling Constants (Hertz) for Trialkylselenonium Ions, Protonated Dialkylselenonium Ions, and Their Corresponding Donor-Acceptor Complexes

cation	solvent system temp, °C	$\delta_{^{77}Se}$	$\delta_{^{13}C}$ ($J_{^{13}C-^{1}H}$)	$^{1}J_{^{77}Se-^{13}C}$
$Me_3Se^{+-}OTf$	SO_2/−40	255	21.78 (147)	51.1
$Me_3Se^{+-}OTf$	CF_3SO_3H/rt	254		
$Me_2EtSe^{+-}OTf$	CF_3SO_3H/rt	285	35.8 (146), $SeCH_2$; 19 (146), $SeCH_3$; 8.8 (131), $SeCH_2CH_3$	52.7, $SeCH_3$; 48.7, $SeCH_2$
$MeEt_2Se^{+-}OTf$	CF_3SO_3H/rt	328	33.5 (146), $SeCH_2$; 16.7 (142), $SeCH_3$; 9.9 (130), $SeCH_2CH_3$	55, $SeCH_3$; 49.5, $SeCH_2$
$Et_3Se^{+-}OTf$	CF_3SO_3H/rt	373	31 (148), $SeCH_2$; 10 (130), $SeCH_3$	52.5
$Me_2HSe^{+-}[FSO_3(SbF_5)]$	magic acid/−60	343	14.6 (150)	57
$Me_2Se^{\delta+\delta-}SbF_5$	SO_2ClF/−60	258	33.4 (150)	68
$Et_2HSe^{+-}[FSO_3(SbF_5)]$	magic acid/−60	399	28.5 (148), $SeCH_2$; 12.0 (132), $SeCH_3$	45
$Et_2Se^{\delta+\delta-}SbF_5$	SO_2ClF/−60	317	44.6 (151), $SeCH_2$; 8.8 (131), $SeCH_2CH_3$	64

Table II. Tellurium-125 and Carbon-13 NMR Chemical Shifts and One-Bond $^{125}Te-^{13}C$ and $^{13}C-^{1}H$ Spin-Spin Coupling Constants (Hertz) for Some Trialkyltelluronium and Protonated Dialkyltelluronium Ions

cation	solvent system/ temp, °C	$\delta_{^{125}Te}$	$\delta_{^{13}C}$ ($J_{^{13}C-^{1}H}$)	$^{1}J_{^{125}Te-^{13}C}$
$Me_3Te^{+-}OTf$	CF_3SO_3H/rt	408	3.76 (145)	143.8
$Me_2EtTe^{+-}OTf$	SO_2/−30	431	18.2 (143), $TeCH_2$; 9.3 (130), $TeCH_2CH_3$; 1.15 (146), $TeCH_3$	149.4, $TeCH_3$; 132, $TeCH_2$
$Me_2HTe^{+-}BF_4$	HF/BF_3/−60	331	−4.5 (148)	124

have remained extremely limited.[10]

The long-lived acidic selenonium and telluronium cations were first prepared by Olah and co-workers[11] by protonation in superacid media. ^{1}H NMR data for these as well as for several trialkylselenonium and trialkyltelluronium fluorosulfates was reported. The most significant observation (^{1}H NMR) was that a consistent trend of increased shielding in onium ions could be established [$\delta_{^{1}H}$: $R_3O^+ > R_3S^+ > R_3Se^+ > R_3Te^+$], reflecting charge delocalization and shielding by heavier atoms.

In relation to our recent work on protosolvated trimethylselenonium and trimethyltelluronium cations in superacid media and their alkylation ability toward aromatics,[12] we have now measured ^{77}Se, ^{125}Te, and ^{13}C NMR chemical shifts and one-bond coupling constants ($^{77}Se-^{13}C$, $^{125}Te-^{13}C$, $^{13}C-^{1}H$) for a range of trialkylselenonium and trialkyltelluronium triflates as well as several acidic dialkylselenonium ions (generated by low-temperature protonation in superacid media) and their corresponding donor-acceptor complexes (SbF_5/SO_2ClF). Our NMR data, gathered in Tables I and II, allow additional new conclusions to be made based upon the observed trends.

The ^{77}Se chemical shift of $Me_3Se^{+-}OTf$ was measured once in liquid SO_2 at −40 °C and once in neat triflic acid at room temperature. The observed difference (1 ppm) supports the idea that the influence of solvent and temperature on the ^{77}Se chemical shift is insignificant.

The ^{77}Se and ^{125}Te NMR chemical shifts of the studied trialkylselenonium and trialkyltelluronium triflates increase systematically as the size of the alkyl ligands increases. This is in line with the data reported by McFarlane,[9,10] O'Brien,[2] and Jones[3] on neutral dialkyl selenides and tellurides, where an increase in the number of methyl groups attached to the α-carbon led to increased deshielding.

The ^{13}C NMR chemical shifts follow the same direction as those of the alkyl protons in that the carbons directly attached to R_3Se^+ and R_3Te^+ are significantly shielded by the heavy atom, and the shielding is more pronounced in R_3Te^+ than R_3Se^+.

The $^{13}C-^{1}H$ coupling constants of the β-alkyl groups in R_3Se^+ are in the range for normal methyls (125–130 Hz), whereas the coupling constants are much larger for the α-methyls (145–150 Hz). A similar observation is made for R_3Te^+.

The ^{77}Se chemical shift of Me_2Se^+H in magic acid is more downfield than that of Me_3Se^+ ($\Delta\delta$ = 91.5 ppm). On the other hand, Me_2Te^+H is more upfield than Me_3Te^+ ($\Delta\delta$ = 77ppm). An inspection of the ^{77}Se and ^{125}Te NMR line widths in the spectra of Me_2Se^+H in magic acid/SO_2 and Me_2Te^+H in HF/BF_3 reveals that the tellurium signal is broader by a factor of 4 as compared to the selenium signal, suggesting that in the weaker acid HF/BF_3 the telluronium ion may not be completely frozen out, and thus the measured chemical shift at −60 °C is slightly underestimated. The ^{13}C NMR of Me_2Te^+H in HF/BF_3 shows the methyl carbon at −4.5 ppm. In addition, a small, as yet unidentified, methyl absorption (quartet in a proton coupled spectrum) at 2.8 ppm is observed, the $^{13}C-^{1}H$ coupling constant (120 Hz) excludes unprotonated Me_2Te (162 Hz) as a possibility.

In agreement with the empirical considerations that a decrease in electron density at selenium leads to increased deshielding, we find that the ^{77}Se chemical shifts of the long-lived acidic selenonium ions Me_2Se^+H and Et_2Se^+H in magic acid are more downfield than their corresponding donor-acceptor complexes $Me_2Se^{\delta+}\rightarrow{}^{\delta-}SbF_5$ and $Et_2Se^{\delta+}\rightarrow{}^{\delta-}SbF_5$.

Interestingly, the ^{13}C chemical shift of the α-methyls change in the opposite direction. The α-carbon is more deshielded in the donor-acceptor complexes than in protonated dialkyl selenides.

$Me_3Se^{\delta+}\rightarrow{}^{\delta-}SbF_5$ is also produced as a byproduct in the protonation of Me_2Se by magic acid/SO_2.[13] But $Et_2Se^{\delta+}\rightarrow{}^{\delta-}SbF_5$ can only by generated independently (SbF_5/SO_2ClF) and is not present in the protonation spectrum of Et_2Se. Attempts to generate a donor-acceptor complex with Me_2Te were not successful. A highly exothermic reaction occurred (even at dry ice temperature), leading to a polytelluride that was not further studied.

The increase in $^{1}J(^{77}Se-^{13}C)$ on going from the selenonium cations to the corresponding donor-acceptor complexes is in agreement with the fact that an increase in the s-character produces an increase in the magnitude of one-bond $^{77}Se-^{13}C$ coupling constants.

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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

$\mathrm{Me_2Se}$ and $\mathrm{Me_2Te}$ 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.

$\mathrm{Me_3Se^{+-}OTf}$, $\mathrm{Et_2MeSe^{+-}OTf}$, and $\mathrm{Me_3Te^{+-}OTf}$ 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. $\mathrm{Et_3Se^{+-}OTf}$ and $\mathrm{Me_2EtTe^{+-}OTf}$ 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 $\mathrm{SbF_5}$. (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 $\mathrm{SO_2}$ (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 $\mathrm{SO_2}$, at −70 °C with efficient vortex mixing to avoid overheating. Dilution of $\mathrm{Me_2Se}$ with $\mathrm{SO_2}$ is rather exothermic. The addition of $\mathrm{SO_2}$ to $\mathrm{Et_2Se}$ is less exothermic, but a pale yellow color develops.

(b) Protonation of $\mathrm{Me_2Te}$ with $\mathrm{HF/BF_3}$. 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 $\mathrm{Me_2Te}$ (ca. 100 mg) was slowly added (vortex). The resulting solution was then saturated with $\mathrm{BF_3}$.

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 $\mathrm{SO_2ClF}$ (vortex). A colorless, homogeneous solution of $\mathrm{SbF_5}$ (2–3-fold excess over the precursor) dissolved in $\mathrm{SO_2ClF}$ (1 mL) was then carefully added to the substrate in $\mathrm{SO_2ClF}$ with vortex mixing while at dry ice–acetone temperature.

Attempted Preparation of $\mathrm{Me_2Te^{\delta+}{\rightarrow}{}^{\delta-}SbF_5}$. Addition of $\mathrm{SO_2ClF}$ (1 mL) to $\mathrm{Me_2Te}$ (150 mg) cooled to −70 °C was extremely exothermic, and a red color developed. Slow addition of $\mathrm{SbF_5}$ in $\mathrm{SO_2ClF}$ 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) $\mathrm{Me_2Se}$ and $\mathrm{Me_2Te}$, 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.

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

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