technique may make it possible to measure such temperatures directly and thereby to test the consistency of both theories.

Finally, the extreme importance of nucleation, itself, in a wide range of scientific and technological disciplines, makes it of special interest to develop and apply the new technique. It is now possible to investigate nucleation in systems particularly free from contaminants and systems (especially in the case of solid-state transitions) that are virtually impossible to probe on such a time scale by other methods.

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Registry No. CCl$_4$, 56-23-5; 1,1,1-trichloroethane, 71-55-6; 2,2-dichloropropane, 594-20-7; *tert*-butyl chloride, 507-20-0; selenium hexafluoride, 7783-79-1.

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Tandem Nucleophilic and Radical Chemistry in the Replacement of the Hydroxyl Group by a Carbon-Carbon Bond. A Concise Synthesis of Showdomycin

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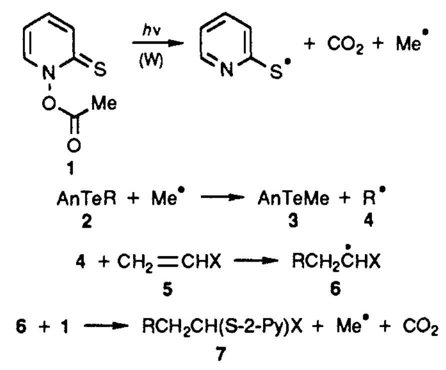
Free-radical reactions have become a popular subject in modern synthetic chemistry.[1] High selectivity and a tolerance for many functional groups make radical reactions easier to carry out than ionic processes. Much elegant radical chemistry has been based on the weakness of the tin-hydrogen bond.[1,2]

In the last six years, we have provided[3] an alternative system for high-yielding reactions, based on acyl derivatives of thiohydroxamic acids. Acyl derivatives of *N*-hydroxy-2-thiopyridone are especially suitable since the reactions are started by tungsten light within a wide temperature range. In addition, on a molar basis, the *N*-hydroxy-2-thiopyridone is at least ten times cheaper than conventional tin reagents.[4]

In this system, the primary source of radicals is the carboxyl function. It would be desirable to adapt the hydroxyl function to the same type of mechanism. There has, indeed, been much interest, especially by Fraser-Reid[5] and Giese,[1,6] for carbohydrate radical chemistry, especially in making the carbon-carbon bond (for other important work, see refs 7 and 8). It seemed to us that the application of organic tellurium chemistry to carbohydrates would permit the generation of a radical at any position where there was a hydroxyl group, and that this could be achieved on the basis of an *N*-hydroxy-2-thiopyridone derivative as light absorber and radical generator. We take advantage of the exceptional nucleophilicity of the anisyl telluride anion and of the exceptional radicophilicity of tellurides in general and of anisyl tellurides in particular.

Scheme I



$$\underset{\mathbf{2}}{\text{AnTeR}} + \text{Me}^{\bullet} \longrightarrow \underset{\mathbf{3}}{\text{AnTeMe}} + \underset{\mathbf{4}}{\text{R}^{\bullet}}$$

$$\mathbf{4} + \underset{\mathbf{5}}{\text{CH}_2{=}\text{CHX}} \longrightarrow \underset{\mathbf{6}}{\text{RCH}_2\dot{\text{C}}\text{HX}}$$

$$\mathbf{6} + \mathbf{1} \longrightarrow \underset{\mathbf{7}}{\text{RCH}_2\text{CH(S-2-Py)X}} + \text{Me}^{\bullet} + \text{CO}_2$$

The hydroxyl group is converted into a suitable leaving group such as mesylate, tosylate, etc. The anisyl telluride anion displaces the leaving group with inversion of configuration, to give an anisyl sugar telluride. Alternatively, an epoxide function can be opened.

Advantage is then taken of facile radical exchange[9] on tellurium(II). However, a "trigger" reaction is needed (Scheme I). The acetyl derivative **1**, on photolysis with tungsten light at room temperature, produces methyl radicals. The methyl radicals react with the telluride **2** to establish a relatively strong Me-Te bond with displacement of the carbohydrate radical **4** (weaker C-Te bond). Radical **4** is a degenerate radical,[10] for by reaction with **2** it regenerates itself. However, as is customary, it is more reactive toward the usual electrophilic olefins than toward the thiocarbonyl of **1**. Hence radical **4** adds to olefin **5** to make a relatively electrophilic radical **6**, which then reacts with the thiocarbonyl function of **1** to afford the product **7** and to re-form the methyl radical and start the cycle again. Methyl anisyl telluride **3** is the other product.

The results summarized in Table I show that the yields are good. After oxidation of the thiopyridine residue in the adduct and the elimination to give trans olefin, a single stereoisomer was obtained in each case.

The occurrence of stereoselective radical reactions with complex molecules can be ascribed to the anomeric effect, the β-bond effect, and steric bulk effects.[1,6] Other recent examples,[11] as well as the work here described, show that very stereoslective radical chemistry can be achieved.

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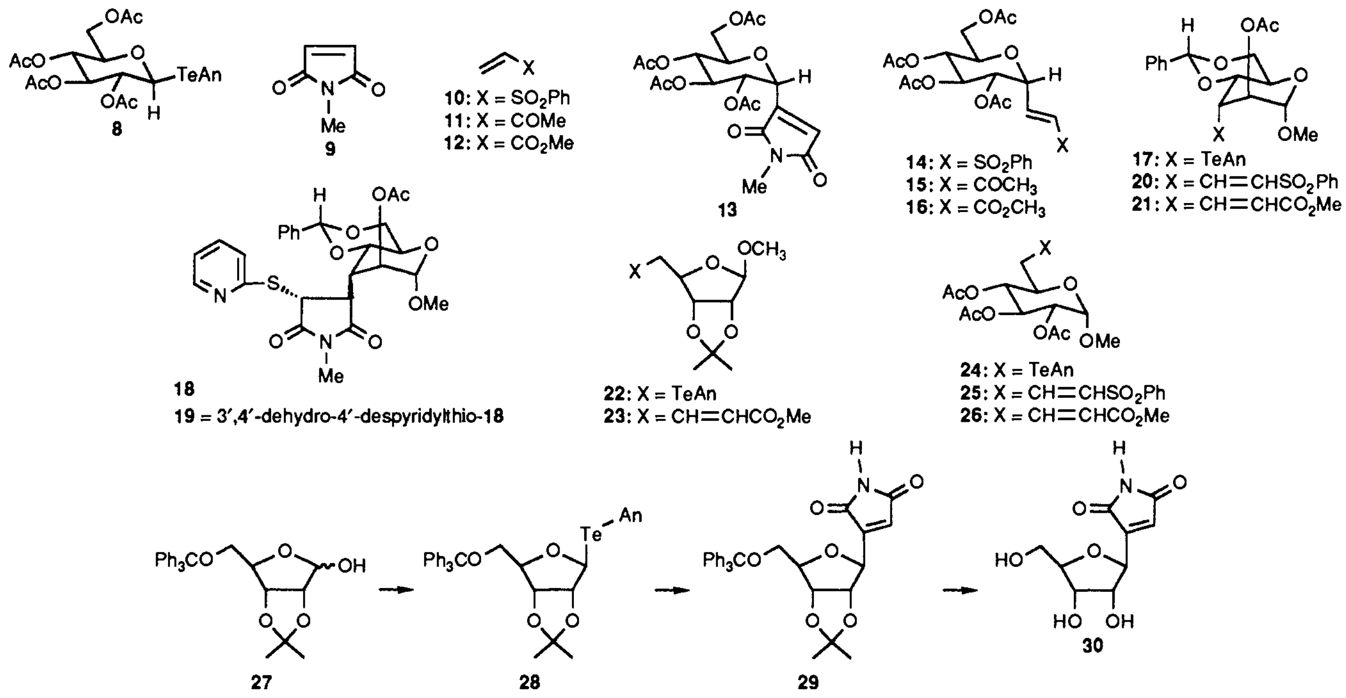
Table I[a,b]

entry	anisyl telluride	olefin	adduct (%)	eliminatn product (%)	characterization of eliminatn product
1	**8**	**9**	(86)	**13** (86)	mp 47–49 °C, $[\alpha]_D$ +98° (*c*, 2.6)
2	**8**	**10**	(80)	**14** (82)	oil, $[\alpha]_D$ +59° (*c*, 1.35)
3	**8**	**11**	(91)	**15** (78)	mp 61 °C, $[\alpha]_D$ +122° (*c*, 1.8)
4	**8**	**12**	(89)	**16** (76)	oil, $[\alpha]_D$ +57° (*c*, 5.8)
5	**17**	**9**	**18** (80)	**19** (76)	mp 149–150 °C, $[\alpha]_D$ +99° (*c*, 5.1)
6	**17**	**10**	(89)	**20** (82)	mp 60–62 °C, $[\alpha]_D$ +70° (*c*, 1.3)
7	**17**	**12**	(84)	**21** (79)	mp 138–139 °C, $[\alpha]_D$ +108° (*c*, 2.9)
8	**22**	**12**	(89)	**23** (81)	mp 84–85 °C, $[\alpha]_D$ −80° (*c*, 1.1)
9	**24**	**10**	(81)	**25** (74)	oil, $[\alpha]_D$ +37° (*c*, 5.0)
10	**24**	**12**	(79)	**26** (75)	oil, $[\alpha]_D$ +39° (*c*, 6.0)

[a] All $[\alpha]_D$ in $CHCl_3$ except entries 9 and 10, where CH_2Cl_2 was used. [b] Typical experiment: To the tellurocarbohydrate (1 mmol) and the appropriate trap (5 mmol) in dry CH_2Cl_2 (4 mL) under argon at 5 °C was added **1** (0.5 mmol). Photolysis with a 150-W W lamp for 10 min was followed by further addition of **1** (0.25 mmol). This was repeated until all the tellurocarbohydrate had disappeared (TLC; about 1.5 mmol of **1** was usually required).

Chart I



The stereochemical assignments in Table I are based on NMR considerations. However, in the case of entry 5, the structure of the adduct (a nicely crystalline compound) was established by X-ray crystallography as shown in **18**.

We completed our study by a short synthesis of the well-known antibiotic showdomycin.[12] The known[13] ribose derivative **27** (Chart I) was mesylated and converted with anisyl telluride anion into **28** (72% overall). Radical addition to maleimide as above gave the β-adduct (78%). Oxidation and elimination afforded the known derivative **29** (82%). Finally treatment with trifluoroacetic acid in tetrahydrofuran gave showdomycin (**30**) (80%), mp 150 °C (needles from acetone–benzene). Professor A. G. M. Barrett and Dr. S. Hoerrner (Northwestern University) kindly showed that this was identical with an authentic specimen.

We have also examined exchange on iodides, a well-known process.[14] When the 6-iodo derivative analogous to **24** was used, there was no exchange and the methyl radical reacted only with the thiocarbonyl of **1** to re-form itself. Similar results were seen with the 6-phenylseleno analogue.[15]

Of course,[3] when no trap is added during the photolysis, the corresponding 2-thiopyridyl derivatives are formed in good yield and with the same stereoselectivity as carbon–carbon bond formation. At the anomeric carbon, these derivatives can be used in glycoside synthesis.[16]

We have also carried out comparable radical chemistry at the 2- and 4-positions of glucose. Details will be given in the full paper.

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