Tetrahedron Vol. 41, No. 19, pp. 4079 to 4094, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

"ONE ELECTRON C-C BOND FORMING REACTIONS VIA ALLYLSTANNANES: SCOPE AND LIMITATIONS"[1]

GARY E. KECK,*‡ ERIC J. ENHOLM,
JOHN B. YATES, AND MICHAEL R. WILEY

Department of Chemistry
University of Utah Salt Lake City, Utah 84112

(*Received in Germany* 13 *February* 1985)

Abstract: Free radical (or "one-electron") methodology for carbon-carbon bond forming reactions using allylstannanes is described in detail. Such reactions have the advantages of tolerating quite complex functionality in the substrate and of being nearly stoichiometric in reagents, and not requiring extensive experimentation for application to new substrates.

Introduction: The general subject of free radical reactions forms an extraordinarily rich topic in organic chemistry. Investigations of such reactions, particularly if one includes at least putative biradicals, have been crucial to the development of physical organic chemistry and our current knowledge and prejudices regarding mechanism. However, despite the availability of this wealth of information, free radical (or "one electron,") methods for the laboratory synthesis of organic intermediates are rare, especially if one restricts attention to those processes which may be regarded as the heart of organic synthesis: the construction of carbon-carbon bonds. Almost invariably, such constructions are made either by the "two electron" union of nucleophiles with electrophiles, or by various cycloaddition processes (e.g. the Diels-Alder reaction, photochemical [2+2] cycloaddition, dipolar [3+2] cycloaddition, etc.) which formally, for our present purposes, can be regarded as biradical dimerization processes. Thus, with a few notable exceptions,[2] free radical methodology has not as yet assumed a position of prominence in organic synthesis.

One might then reasonably ask why such a situation exists. An obvious answer, particularly given the current emphasis on stereoselectivity in organic synthesis, is that free radical reactions are generally regarded as possessing no intrinsic stereochemistry. However, the alkylation of ketone enolates also is devoid of intrinsic stereochemistry, yet such carbon-carbon bond forming reactions can be found in almost every total synthesis of a complex natural product. Thus this particular issue can be summarily dismissed.

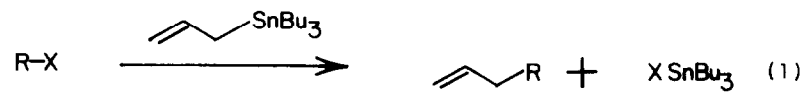
Perhaps more serious is the problem of chemoselectivity. Many organic chemists tend to view free radical reactions with suspicion in this regard, and are somewhat biased toward regarding free radical processes as rather indiscriminate. In this context, it is very useful to divide one electron reactions into two general categories: those which are chain processes, and those which are not. Most reactions in current use, including the title process, fall into the former category, which, unfortunately, requires some special efforts on the part of the investigator to ensure success. In free radical chain processes, interruption of a chain can have disastrous consequences for the overall rate of consumption of starting material, as compared with more common two electron processes involving nucleophile-electrophile pairings. Thus, for example, adventitious oxygen will almost invariably be more

deleterious to a free radical chain process than to an enolate alkylation, although the reactive intermediates involved in both cases may be intercepted by oxygen. More importantly, to design a successful, high yielding, free radical chain process, one must control a number of reaction processes, not just one. Of crucial importance are:

1. Specific generation of initiator radicals,
2. Selective, low energy pathways for the production of substrate radicals,
3. Chain carrying steps with reagents which preclude the formation of highly reactive, indiscriminate radicals,
4. Reasonable termination steps to produce innocuous by-products which do not disturb the chain.

The constraints delineated above are rather formidable, however, they are met in the free radical allylation of suitable substrates using allylstannanes, as shown in equation 1 below.[3] We detail here our studies on such reactions with an emphasis on:

1. Precursors to the carbon centered radicals which carry the chain,
2. Structure-reactivity relationships in the allylstannane partners,
3. Scope of the reaction process with respect to functionality present in the substrate, and
4. Stereochemistry.



(1)

Results

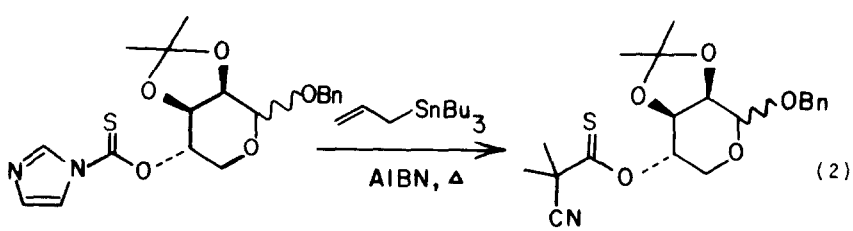
Our initial investigations on the viability of free radical allyl transfer reactions via reaction of allyltri-n-butylstannane with carbon centered radicals began with very simple alkyl halides where both starting materials and the desired products were readily available. No attempts to determine isolated yields were made in these cases, instead, yields were detemined by VPC analysis using internal standards; the response factors for the flame ionization detectors were determined using mixtures of internal standard and authentic samples of products. These reactions were conducted using azo-bis-isobutyronitrile (AIBN) as initiator, at 80°C in toluene. It was found that good to excellent yields of products were obtained using both allyltri-n-butylstannane or methallyltri-n-butylstannane. Results from this initial investigation are tabulated in Table I.

Having established that the expected reaction process could be realized in satisfactory yields with such simple substrates, attention was then turned to investigations in more complex systems. Of particular interest in this regard, given the requirement that the substrate be a precursor to a carbon centered radical, were materials available by various oxidative additions to alkenes, such as halolactones, haloethers, and the corresponding selenide derivatives.[4] As shown in Table II (vide infra) such materials can be utilized without complication in such free radical allylation reactions. The lack of reactivity of the phenylsulfide derivative 7c (where both the corresponding bromide and phenylselenide were used successfully) should be noted.

Also apparent from the data in Table II is the extraordinary tolerance of the process to a wide variety of functionality which would be expected to be incompatible with "two electron" approaches to achieving the same net bond construction. The application of the method to β-oxygenated systems has already been noted.[1] Substrates containing esters or lactone functions (entries 7a-c, 9, 15, 17), sulfonate esters (entry 15b), and epoxides (entry 17) have all been used without complication in such reactions. It should be noted that simple olefins are also, in general, compatible with such a process, as evidenced by the high isolated yields of products containing this functional group.

Table II contains three entries (15a, 15b and 17) demonstrating chain extension at C-6 in highly functionalized pyranosides. In this context, the utility of the method of Hanessian[5] in securing such deoxy-bromo derivatives should be mentioned, as it provides a particularly expedient approach to such materials.

The results obtained for allylation or methallylation at interior positions in such pyranosides or furanosides, including the anomeric center, are also summarized in Table II. For functionalization at interior positions other than the anomeric center, the use of various thioacylderivatives as precursors to the requisite carbon centered radicals, as developed by Barton for deoxygenation by reaction with tri-n-butyltin hydride,[6] proves especially convenient. In our experience, the highest overall yields are obtained most conveniently by acylation of the alcohol with phenylchlorothioformate, followed by reaction with allyltri-n-butylstannane using photochemical ($\lambda > 300$ NM) initiation. The corresponding thioacylimidazoles and xanthates were also examined using a common substrate (note entries 19a, b, and c in Table II). The thioacylimidazole proved rather difficult to obtain in pure form, which contributed, albeit only in part, to the lower yield obtained with substrate 19b than with thionocarbonate 19c. Chemical initiation with AIBN was also investigated with the thioacylimidazole derivative 19b. However, it proved very difficult to initiate the reaction in this case, and large amounts of initiator were required to consume starting material. The major product isolated in this instance was not the desired allylated material, but rather a compound (note equation 2 below) which is presumably formed by addition of the 2-cyanopropyl radical to the thioacylimidazole at carbon, rather than sulfur, followed by scission of the imidazole moiety.



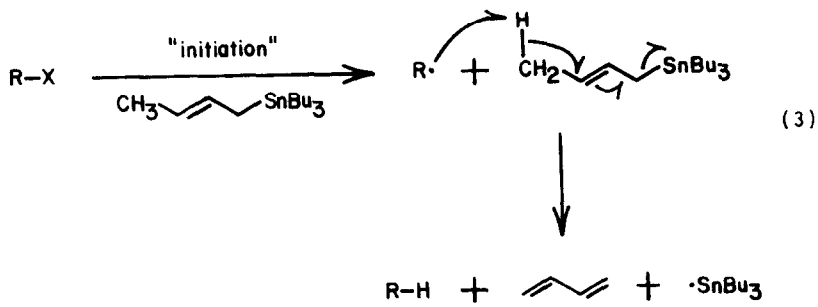
(2)

For allylation reactions at the anomeric center, the appropriate chlorides or bromides may be employed as substrates (entries 21, 23) provided that these intermediates are reasonably stable and can be obtained in pure form. Unfortunately, in our experience, this is seldom the case. For example, 1-chloro 1-deoxy-2,3-isopropylidenelyxopyranose is far too unstable to be used

successfully in such reactions. The various thioacyl derivatives previously discussed also suffer from rather low hydrolytic stability, and are difficult to obtain in pure form, which complicates their use in such reactions. For example, the best overall yield using such thioacyl functionality with the lyxose system (note structure 29) was 50% for the two step sequence of acylation with phenylchlorothioformate followed by reaction with allyltri-n-butylstannane.

Far better results may be obtained using readily available thiophenylglycosides. These hydrolytically stable materials are easily prepared, in high yield, by reaction of a suitably protected pyranose or furanose with diphenyldisulfide and tri-n-butylphosphine in methylene chloride, and are easily purified by silica gel chromatography. Reaction with allyl or methallyltri-n-butylstannane, using photochemical initiation, then affords C-allyl or C-methallyl glycosides in high yield.[7] (Note entries 25, 27, and 29, in Table II). It should be noted that this reactivity appears unique to α-oxygenated (or, perhaps, otherwise "activated" thiophenyl derivatives), since substrate 7d (Table II) does not undergo free radical allylation. The lack of reactivity of such materials toward reduction with tri-n-butyltinhydride has also been noted by Vedejs.[8]

Several attempts were made to utilize crotyltri-n-butylstannane in such reactions; however, using either of the general protocols described above, starting materials were recovered essentially unchanged. Considerably more forcing conditions, e.g. xylene or chlorobenzene at reflux, using di-tert-butylperoxide as initiator, were required for reaction in these cases. However, the observed products were not those expected for the allyl transfer process, but instead corresponded to simple reduction, as shown in equation 3 below.



(3)

Since no evidence could be amassed either for contamination of the crotyltri-n-butylstannane by tri-n-butyltin hydride, or for the formation of tri-n-butyltin hydride under the reaction conditions in the absence of substrate, it appears that crotyltri-n-butylstannane reacts with carbon centered radicals by transfer of a hydrogen from the methyl group, followed by scission to produce the reduced product, butadiene, and tri-n-butylstannyl radical. Evidence for the production of butadiene was obtained by trapping with bromine after completion of reaction for the case of 1-bromodecane.[9]

In one case, we examined the use of 3-(tri-n-butylstannyl)-1-butene in such reactions. As this material is essentially impossible to obtain in pure form, due to its facile isomerization to crotyltri-n-butylstannane, a mixture (ca. 4:6) of these two materials was utilized. With substrate 13, a 1:1

mixture of products corresponding to reduction and allyl transfer (with allylic inversion) from the 3-(tri-n-butylstannyl)-1-butene were obtained in 50% isolated yield using the thermal (toluene, 80°, AIBN initiation) protocol previously described. Since crotyltri-n-butylstannane was shown to be unreactive under these conditions, it would appear that 3-(tri-n-butylstannyl)-1-butene is an even more powerful hydrogen donor than crotyltri-n-butylstannane. In any event, it does not appear that stannanes having this substitution pattern will prove useful in such allylation processes. Thus, to date, only the parent allyltri-n-butylstannane or derivatives with substitution in the 2 position of the allyl unit have been used without complication in these reactions.

It should be apparent from the foregoing discussion that free radical allylations using allyl or methallyltri-n-butylstannane are extraordinarily tolerant of complex functionality in the substrate. Unfortunately, the scope of the reaction with respect to structure of the stannane is much more restricted, as mentioned above. Nonetheless, the utility of allyl and methallyl units with respect to further chemical transformations is sufficiently great that the method is still a very powerful one.

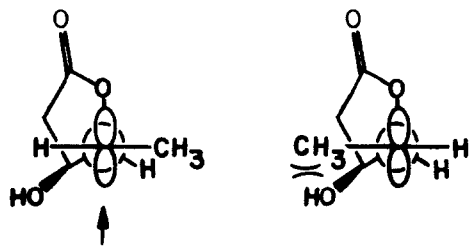
In many instances, good stereochemical control can be achieved in the introduction of such substituents. The observed products may in general be predicted by assuming preferential addition of allyltri-n-butylstannane to the less hindered face of an intermediate radical, and good stereoselectivity in such reactions appears to require a significant steric bias in the substrate. The products obtained from mannose derivatives 23 and 25, lyxose derivative 19c, and lyxose derivative 29 may all be rationalized on this basis, and the degree of stereocontrol realized (> 95:5) is very high. The stereoselectivity obtained with ribose derivative 27 is somewhat lower (4:1), but still in accord with preferential addition to the convex face of the substrate. It should also be noted that results recently reported by Danishefsky and Webb in a nitrogen containing system are also in accord with these observations.[10]

For one substrate containing a conformationally locked six-membered ring (13, Table II), exclusive equatorial incorporation of allyl was observed. It may be that steric factors are controlling in this case, or that other effects, presently unknown, are responsible for the high degree of stereoselectivity observed. For instance, in this case, an oxygen substituent is present adjacent to the radical center, and allylstannane addition proceeds preferentially syn to the oxygen substituent. Although the ramifications of this observation remain to be fully explored, it does appear that β oxygenated substrates are unusual in another regard. We have not attempted any absolute or relative rate determinations to date, but β oxygenated substrates appear to be more reactive than one might expect based on their structure, particularly for primary cases. Barton has explicitly noted parallel behavior for tin hydride reductions of β oxygenated substrates.[11]

Thus we have been led to examine the extent to which such rate phenomena may have stereochemical consequences in such free radical allylation reactions. Halolactone 9 and haloether 11 represent rigid six-membered ring systems with the β oxygen atom locked in an axial position. Both substrates show low stereoselectivity in free radical allylation using either photochemical or thermal initiation, favoring equatorial incorporation of allyl by about

1.7:1. Higher selectivity is observed with bromohydrins 31 and 33 which preferentially yield trans products with stereoselectivities of 10:1 (67% yield) and 4:1 (74% yield), respectively, using photochemical initiation. There is also surprisingly little change in stereoselectivity observed using various protected derivatives of 31 and 33. Thus, the tert-butyldimethylsilyl, tert-butyl diphenylsilyl, and benzoate derivatives of the five-ring bromohydrin 31 gave trans-cis selectivities for free radical allylation of 7:1, 11:1, and 7:1, respectively, using photochemical initiation, whereas the analogous derivatives of the six-ring bromohydrin 33 afforded trans-cis ratios of 2:1, 2:1, and 3:1, respectively. Although acyclic systems possessing β-oxygen substituents have yet to be examined thoroughly with respect to stereochemistry, it does not appear likely at this point that significant levels of stereoselectivity will be realized in such systems. For example, we have examined free radical allylation of the known[12] iodolactone 35 in this regard, and find that a 1.6:1 mixture of diastereomeric products is produced upon free radical allylation using photochemical initiation. If the rate phenomena associated with β-alkoxy substituted radicals were the result of a preferred orientation of the C-O σ bond with respect to the adjacent p orbital, then one might have expected considerably higher stereoselectivity in this case. For instance, one could envision limiting geometries in which the C-O bond and p orbital were oriented either parallel or orthogonal to each other. A coplanar arrangement of C-O and the orbital containing the odd electron (note figure I below), assuming staggering of bonds in the transition state,[13] would suggest that reaction as indicated in conformer A would be strongly preferred due to severe $A_{1,3}$-like interactions in conformer B.

Figure I



Orthogonal alignment of C-O and the p orbital would not be expected to exhibit as clear-cut a steric biasing, and reaction through such conformations may be responsible for the low stereoselectivities observed. However, further investigations in this regard, both computational and experimental, are clearly needed.

Experimental details for representative examples described herein are included in the experimental section. However, it is important to note that all of the cases examined to date have been performed precisely according to one of the general protocols (Methods Δ and hν, Table II) described earlier. In general, the only identifiable side reaction observed is the formation of small amounts of reduction products in some cases. Reduction is most generally observed with substrates which possess poor solubility in toluene, and can be minimized by employing benzene as solvent. Along these lines, it should be noted that the requisite stannanes are readily available from inexpensive starting materials, as detailed in the Experimental Section. However, these clear colorless liquids may become cloudy upon prolonged storage and the

impurities produced appear to inhibit the allylation reaction. Passage of a hexane solution of the stannane through a plug of silica gel is sufficient to remedy this problem.

We have also observed that better results in the thermally initiated reactions are obtained using oil baths rather than heating mantles, and that optimal results are obtained when the level of solution inside the flask is above the level of the oil (80°C) outside the flask. Perhaps local overheating may lead to the production of impurities which serve as inhibitors of the chain process. Of course, all such reactions must be thoroughly degassed to achieve the best results.

One experimental problem to be faced at the completion of such reactions is the removal of tin containing materials from the desired products. A number of procedures prove useful here. For reasonably polar compounds, partitioning the crude product between acetonitrile and pentane will generally remove the bulk of the tin containing compounds. Alternatively, or as a compliment to such purification, stirring with aqueous KF will convert tin halides, etc. to stannyl fluorides, which are very insoluble and can be removed by filtration. Filtration through basic alumina is also very effective in removing such materials. Ultimately, the products described herein for which isolated yields are given were obtained in pure form by chromatography over silica gel. However, this is often problematic if recourse is not made to one of the methods mentioned earlier prior to chromatography, due to the pronounced tendency of many organotin compounds, tin halides, particularly, to "streak" on silica gel chromatography.

Finally, it is important to note that reaction times specified for the photochemical procedure are intended to serve only as a rough guide as to what one may expect. Times for completion of reaction using this procedure will clearly depend heavily upon the arrangement of a particular set-up, and, in particular, upon the age and condition of the lamp and immersion well used for the reaction.

In summary, we have found such a "one electron" approach to the formation of carbon-carbon bonds to be a very general, reliable, and powerful process in organic synthesis. The methodology described above provides a reliable and generally high yielding method for the construction of carbon-carbon bonds, which is notable for its tolerance of complex functionality. It should also be noted that the method is a powerful compliment to various oxidative addition reactions, such as halolactonization and selenolactonization, particularly in view of the high degree of stereocontrol which may be achieved in such processes. Such reactions have, to date, been employed successfully in our laboratories in the context of total syntheses of (±)-perhydrohistrionicotoxin[14] and (+)-pseudomonic acid C,[15] and have played a key role in our synthetic approach to (+)-compactin as well.[16] Further progress quite clearly requires a greater understanding of the factors which control the stereochemistry of such reactions, extension to intramolecular cases, utilization of such stannanes as terminators for important free radical rearrangements and cyclizations, and a solution to the structural limitations on the allylstannane reactants imposed by their very facile allylic rearrangement. Efforts in these regards are in progress in our laboratories and will be reported in due course.

Experimental Section

General

Melting points were recorded on a Mel-temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Acculab 3 IR spectrometer and are reported in cm^{-1}. ^1H NMR spectra were recorded at 90 MHz using a Varian EM-390 or at 300 MHz using a Varian SC-300. ^{13}C NMR were recorded at 20 MHz using a Varian FT-80 or at 75 MHz using a Varian SC-300. Chemical shifts are in parts per million downfield from internal Me_4Si; coupling constants are given in Hertz. Solvents were purified as follows: toluene, ether, and tetrahydrofuran by distillation from benzophenone ketyl under argon; hexanes and ethyl acetate by distillation; methylene chloride and DMF by distillation from calcium hydride. Mass spectra were recorded on a VG Micromass 7070 in the electron impact or chemical ionization (CI) mode with the indicated reagent gas. Elemental analyses were performed by Galbraith Laboratories. All reactions described were carried out under an atmosphere of nitrogen or argon. Unless otherwise indicated, all yields reported are isolated yields of material judged homogeneous by thin-layer chromatography and NMR spectroscopy and, for crystalline solids, material having the indicated melting point. Thin-layer chromatography was performed on Merck 0.25-mm glass silica gel plates; visualization of developed plates was by fluorescence quenching and staining with phosphomolybdic acid. Column chromatography was performed using Merck or Davison silica gel 60 (60-240 mesh). MPLC refers to medium-pressure liquid chromatography over Merck silica gel 60 (230-400 mesh) with an FMI lab pump operated at 60-100 psi, Altex columns, and a UV detector and fraction collector. All capillary VPC analyses reported employed a Varian 3400 VPC and Vista 402 Data System; the column utilized was a 30 M J & W DB-5. For all reactions specifying "irradiation" or "photolysis", the light source was a 450 W Hanovia lamp equipped with a Pyrex filter.

Allyltri-n-butylstannane: Allyltri-n-butylstannane is available from Aldrich Chemical Co. or it can be prepared easily and inexpensively by the general method of Seyferth and Weimer.[17] Thus, to a mechanically stirred suspension of magnesium turnings (4.1 g, 171 mmol) in anhydrous THF (20 mL) was added dropwise at 5°C a solution containing allylchloride (11.8 g, 154 mmol) and tri-n-butylstannyl chloride (25 g, 76.8 mmol) in 50 mL of THF. After the addition was completed, the reaction was heated to reflux (cautiously) for 2 h, then cooled to 0°C in an ice bath. Careful slow quenching with aqueous NH_4Cl (satd), was followed by filtration under aspirator vacuum and removal of THF in vacuo. Ether was added and the organic phase was separated, washed with 2 x 100 mL of water, once with brine, and dried over Na_2SO_4. Concentration in vacuo afforded a yellow oil which was filtered through silica gel to yield 22.5 g (90%) of a colorless oil. The yellow oil can also be distilled (88°C/0.2 mm) to purity. This procedure has been scaled up to afford 200 g lots without difficulty. ^1H NMR ($CDCl_3$) δ 6.1 (m, 1 H), 5.0-4.6 (m, 2 H), 1.8 (d, 2 H, J =9), 1.65-1.05 (18 H), 1.0-0.7 (9 H); IR (neat) 2950, 1620, 1190, 880 cm^{-1}.

Methallyltri-n-butylstannane: This material was prepared from 3-chloro-2-methylpropene and tri-n-butylstannyl chloride by the same method as delineated above with similar results: ^1H NMR ($CDCl_3$) δ 4.6 (br, 2 H), 1.9 (s, 2 H), 1.8 (s, 3 H), 9.6-1.0 (18 H), 0.9 (m, 9 H); IR (neat) 3060, 2950, 1460, 855 cm^{-1}.

Preparation of 2,2-Diphenyl-5-bromo-4-pentanolide (7a). A solution containing 2,2-diphenyl-4-pentenoic acid (2.4 g, 9.6 mmol) and KBr (1.1 g, 9.6 mmol) in 10 mL of saturated aqueous $NaHCO_3$ was cooled in an ice bath and titrated with a bromine solution (ca. 2.5 mL of 3.9 M in CH_2Cl_2) until the orange color persisted. The mixture was stirred 5 min, CH_2Cl_2 was added and the layers separated. The organic layer was washed with aqueous $Na_2S_2O_3$, water, and dried over anhydrous $MgSO_4$. Concentration in vacuo gave 3.0 g (95%) of a colorless solid: mp 88-90°C; R_f 0.19 (15% THF-hexanes); NMR ($CDCl_3$) δ 7.4 (m, 10 H), 4.55 (m, 1 H), 3.55 (d, J = 6, 2 H), 3.15 (dd, J = 12, 5, 1 H), 2.75 (dd, J = 12, 9, 1 H); IR ($CHCl_3$) 3050, 1770, 1600, 1495, 1450, 1330, 1170, 1095, 1030, 970, 910 cm^{-1}. Recrystallization from CH_2Cl_2-hexanes gave an analytical sample: Anal. ($C_{17}H_{17}O_2Br$) C, H.

Preparation of 2,2-Diphenyl-5-phenylselenyl-4-pentanolide (7b). A suspension of 2,2-diphenyl-4-pentenoic acid (0.50 g, 2.0 mmol) in CH_2Cl_2 (2 mL) was cooled in an ice bath and triethylamine (0.40 g, 4.0 mmol) was added. After the solid acid had dissolved, phenylselenyl chloride (0.46 g, 2.4 mmol) was added as the solid. Examination by thin layer chromatography revealed the absence of starting material and the solution was washed with water. After concentration in vacuo, chromatography over silica gel eluting with CH_2Cl_2 gave 0.75 g (92%) of the desired product as a yellow oil: R_f 0.22 (15% THF-hexanes); NMR ($CDCl_3$) δ 7.60-6.80 (m, 15 H), 4.45 (m, 1 H), 3.25 (dd, J = 13, 5, 1 H) 3.10 (dd, J = 12, 5, 1 H), 2.95 (dd, J = 13, 7, 1 H), 2.60 (dd, J =

12, 10, 1 H); IR (neat) 3060, 1740, 1580, 1490, 1470, 1450, 1440, 1160, 1000 cm^{-1}. Anal. ($C_{23}H_{22}O_2Se$) C, H.

Preparation of 2,2-Diphenyl-5-Phenylthio-4-pentanolide (7c). To a suspension of NaH (59 mg, 2.5 mmol) in 1:1 THF-DMF (2 mL) at 0°C was added thiophenol (291 mg, 2.6 mmol) and the reaction was stirred for 0.5 h. Bromide 7a (680 mg, 2.1 mmol) in THF (3.0 mL) was added, the bath was removed, and the solution stirred for 3 h at room temperature. Examination by thin layer chromatography revealed the absence of starting material, and the reaction was quenched by the cautious addition of water. Ethyl acetate was added and the organic layer was washed twice with water, once with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Chromatography over silica gel eluting with 20% THF-hexanes gave 630 mg (85%) of the sulfide: R_f 0.58 (35% THF-hexanes); NMR ($CDCl_3$) δ 7.3 (m, 15 H), 4.36 (m, 3.10 (dd, J = 13, 6, 2 H), 2.59 (dd, J = 17, 9, 2 H) mass spectrum (CI isobutane), M/Z (rel intensity) 360.1 (35), 209.0 (14), 207.1 (14), 193.1 (27), 178.0 (19), 165.1 (25), 129.0 (100), 123.0 (15),115.1 (17), 103.1 (68), 91.1 (95), 77.0 (28).

Preparation of 2,2-Diphenyl-7-octen-4-olide (8).

Thermal initiation: A thoroughly degassed (argon) solution of selenide 7b (223 mg, 0.55 mmol), allyltri-n-butylstannane (365 mg, 1.10 mmol) and AIBN (18 mg, 0.11 mmol) in 1.1 mL of benzene was heated at 80°C for 10 h. Examination by thin layer chromatography revealed the absence of 7b. The solvent was removed in vacuo and the resulting material was chromatographed over silica gel eluting with 10% ethyl acetate-hexanes to give 132 mg (79%) of lactone 8: R_f 0.57 (10% ethyl acetate-hexanes); NMR ($CDCl_3$) δ 7.5 (m, 10 H), 6.0 (m, 1 H), 5.2 (m, 2 H), 4.5 (m, 1 H), 3.1 (d of d, J= 5, 15, 1 H), 2.65 (d of d, J=15, 12, 1 H), 2.2 (m, 2 H), 1.8 (m, 2 H); IR ($CHCl_3$) 3000, 2940, 1725, 1640, 1600, 1500, 1450, 1265, 1180 cm^{-1}; Anal.: ($C_{20}H_{20}O_2$) C, H.

Photochemical initiation: A thoroughly degassed (argon) benzene solution (1.0 mL) containing selenide 7b (195 mg, 0.48 mmol) and allyltri-n-butylstannane (320 mg, 0.79 mmol) was placed in an argon flushed Pyrex glass tube and irradiated for 8 h. Examination by thin layer chromatography showed complete consumption of 7b and the reaction was worked up as described for the thermal case to yield 105 mg (75%) of lactone 8.

Bromide 7a afforded allyl product 8 in 88% yield thermally and in 82% yield by photo initiation. The corresponding sulfide 7c did not react to afford 8 under these conditions.

Preparation of thionocarbonate 19c. A solution of 1-O-benzyl-2,3-isopropylidene-L-lyxose[15] (12.90 g, 0.0460 mol) in 100 mL of THF was cooled to -78°C, and 1.4 M MeLi in ether (36.1 mL, 0.0500 mol) was added dropwise over a 15 min period. After stirring for 15 min at -78°C phenyl chlorothionocarbonate (7.64 mL, 0.055 mol) was added dropwise by syringe over a 10 min period. The resulting solution was allowed to warm to room temperature over 45 min, then water (70 mL) was added and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic layers were dried and concentrated to an oil which was chromatographed over silica gel (30% ether-hexanes) to yield 17.1 g (90%) of a thick straw colored oil as a mixture of anomers, R_f 0.54, 0.65 (35% THF-hexanes); higher R_f anomer (isolated by chromatography over silica gel): 90 MHz ^1H NMR ($CDCl_3$) δ 7.30 (m, 10 H), 5.50 (m, 1 H), 4.95 (d, J = 3, 1 H), 4.50 (center of AB q, J = 12, 2 H), 4.45 (m, 1 H), 4.20 (d of d, J = 3, 6, 1 H), 3.90 (m, 2 H), 1.45 (s, 3 H), 1.30 (s, 3 H); lower R_f anomer (isolated by chromatography over silica gel) 90 MHz ^1H NMR ($CDCl_3$) δ 7.30 (m, 7 H), 6.75 (m, 1 H), 4.70 (center of AB q, J = 12.0, 2 H), 6.75 (d, J = 4.5, 1 H), 4.40 (m, 1 H), 3.95, (d of d, J = 4.5, 6.0, 1 H), 3.75 (m, 2 H), 3.40 (d of d, J = 7.0, 13.5 1 H), 1.40 (s, 3 H), 1.30 (s, 3 H); IR (neat) 3300-3500 (br), 3030-3060, 2760-2980, 1600 (s), 1200, 860, 770, 750, 690 cm^{-1}; mass spectrum (CI isobutane) 417.2 (M + 1, 2.5), 309 (M - OCH_2Ph, 36), 231 (36), 126 (41), 107 (25), 91 (100).

Preparation of xanthate 19a. To a solution of one anomer of 1-O-benzyl-2,3-isopropylidene-L-lyxose[15] (0.143 g, 0.51 mmol) in 10 ml of THF at -78°C was added n-BuLi (320 μl of 1.6 M in hexanes, 0.560 mmol) slowly via syringe over 10 min followed by carbon disulfide (0.116 g, 1.53 mmol). The mixture was warmed to 23°C and, after 0.5 h, CH_3I (94 μl, 1.53 mmol) was added. The reaction was quenched with 30 mL of water after an additional hour. The aqueous layer was extracted with ether (3 x 50 ml) and the organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude oil was chromatographed over silica gel to yield 165 mgs (88%) of a thick yellow oil: R_f 0.57 (35% THF-hexanes), ^1H NMR ($(CD_3)_2CO$) δ 7.30 (m, 5 H), 5.80 (m, 1 H), 4.90 (m, 1 H,), 4.68 (center of ABq, 2 H, J = 13 Hz), 4.40 (m, 1 H), 4.15 (d of d, 1 H, J = 3, 6 Hz), 3.80 (m, 2 H), 2.53 (s, 3 H), 1.38 (s, 3 H), 1.27 (s, 3 H); IR (neat) 3030, 1265, 750 cm^{-1}. ^{13}C NMR ($(CD_3)_2CO$) δ 205.96, 129.20, 128.95,

128.85, 128.58, 109.91, 98.51, 78.85, 75.99, 74.71, 69.94, 58.89, 27.93, 26.35, 19.10.

Preparation of thioacylimidazole 19b. A solution of two anomers of 1-O-Benzyl-2,3-isopropylidene-L-lyxose[15] (15.50 g, 0.0553 mol) and thiocarbonyl diimidazole (14.85 g, 0.083 mol) in 350 mL of THF was refluxed for 6 h. Hexanes (200 ml) were added and the organic layer was washed with water (2 x 150 ml). The aqueous layer was back extracted with ether (2 x 100 ml) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resultant oil was passed through a plug of silica gel with ether to remove imidazole and give 19.88 g (92%) of a colorless oil: R_f 0.42 (both anomers) (35% THF-hexanes), ^1H NMR ($CDCl_3$) δ 8.60 (bs, 1 H), 7.80 (bs, 1 H), 7.51 (m, 5 H), 7.22 (bs, 1 H), 5.80 (m, 1 H), 5.30 (d, 1 H, J = 3 Hz), 5.91 (center of ABq, 2 H, J = 7 Hz), 4.78 (t, 1 H, J = 3 Hz) 4.60 (m, 1 H), 4.30 (m, 1 H) 4.02 (m, 1 H), 1.40 (m, 6 H); IR (neat) 2820-3700 (s, br), 1630 (s, br).

Preparation of allyl adduct 20 from thionocarbonate 19c. Thionocarbonate 19a (11.16 g, 26.8 mmol) was placed in a Hanovia photolysis apparatus along with 17.68 g (53.6 mmol) of allyltri-n-butylstannane and 54 mL of toluene. After thoroughly degassing the solution with argon, it was irradiated for 65 h at 23 °C. Solvents were removed in vacuo and the crude product was chromatographed over silica gel (5% ether-hexanes) to yield a total of 6.25 g (80%) of a colorless oil: R_f 0.36, 0.29 (20% ether-hexanes); higher R_f anomer (isolated by chromatography over silica gel) mp 43-44 °C; $[\alpha]_D^{23}$ = -70.3 (C = 0.0774, CH_2Cl_2) 300 MHz ^1H NMR ($CDCl_3$) δ 7.32 (m, 5 H), 5.74 (m, 1 H), 5.00 (m, 2 H), 4.86 (d, J = 2.1, 1 H), 4.61, (center of AB q, J = 12.0, 2 H), 3.95, (m, 2 H), 3.58 (d of d, J = 3.8, 12.0, 1 H), 3.48 (d of d, J = 8.8, 12.0, 1 H), 2.33 (m, 1 H), 1.95 (m, 2 H), 1.44 (s 3 H), 1.32 (s, 3 H); 75 MHz ^{13}C NMR ($CDCl_3$) δ 137.6, 136.0, 128.7, 128.4, 128.1, 117.2, 109.0, 98.2, 76.1, 74.2, 69.3, 61.4, 38.1, 34.1, 28.2, 26.5; lower R_f anomer (isolated by chromatography over silica gel) 300 MHz ^1H NMR ($CDCl_3$) δ 7.36 (m, 5 H), 5.78 (m, 1 H), 5.06 (m, 2 H), 4.72 (center of AB q, J = 11.8, 2 H), 4.48 (d, J = 5.7, 1 H), 4.31 (d of d, J = 3.2, 6.3, 1 H), 3.96 (d of d, J = 6.1, 11.6, 1 H), 3.74 (d of d, J = 6.1, 11.6, 1 H), 3.45, (m, 1 H), 2.18 (m, 1 H), 2.02 (m, 2 H), 1.36 (s, 3 H), 1.32 (s, 3 H); 75 MHz ^{13}C NMR ($CDCl_3$) δ 137.9, 135.7, 128.7, 128.5, 128.3, 117.1, 109.4, 100.1, 75.7, 74.0, 70.1, 64.3, 35.7, 32.3, 27.5, 25.7; IR (neat) 3020, 3060 (ws), 2920, 1640, 1375, 1080, 735, 700 cm^{-1}; mass spectrum (CI isobutane) 305 (M + 1, 5), 197 (M - OCH_2Ph, 100), 139 (47), 91 (56); exact mass calcd for $C_{18}H_{24}O_4$ 304.1674, found 304.1656. Anal. ($C_{18}H_{24}O_4$) C, H.

Preparation of 20 from thioacylimidazole 19b.

Photochemical initiation: The thioacylimidazole derivative (19.60 g, 50.0 mmol) was placed in an immersion well photolysis apparatus along with 100 mL of toluene and allyltri-n-butylstannane (33.1 g, 100 mmol), and the solution was degassed for 1 h with argon. The solution was then photolysed until complete reaction was observed by TLC (ca. 12 h) and then concentrated in vacuo to give a semi-solid crude mixture. Chromatography over silica gel gave 8.80 g (55%) of 20 as a thick colorless oil.

Preparation of 20 from xanthate 19a.

Thermal initiation: The xanthate 19a (84 mgs, 0.23 mmol) was placed in a 10 mL pear flask along with AIBN (7.8 mgs, 0.0046 mmol) and 0.50 mL of toluene. To this mixture was added allyltri-n-butylstannane (149 mgs 0.46 mmol) and after degassing for 15 min the reaction was heated at 80°C overnight. The resulting mixture was concentrated in vacuo and chromatographed over silica gel to render 8.7 mg (13%) of 20 as a thick colorless oil.

Photochemical initiation: The xanthate derivative 19a (196 mgs, 0.53 mmol) was placed in a 5.0 mm NMR tube along with 1.0 mL benzene and 1.06 mmol of allyltri-n-butylstannane and irradiated until no starting material remained by TLC analysis. Crude products were concentrated in vacuo and chromatographed over silica gel to render 100 mgs (62%) of 20 as a thick colorless oil.

Preparation of Allyl Compound 14.

Photochemical initiation: A solution of bromide 13[14] (541 mg, 2.09 mmol) and 2 equivalents of allyltri-n-butylstannane (1.38 g, 4.18 mmol) in dry toluene (4.0 mL) was degassed with argon for 15 min. The solution was then irradiated for 6 h. After removal of the toluene in vacuo, the crude material was partitioned between acetonitrile and pentane. The acetonitrile was removed in vacuo to give the crude allyl compound. Further purification was accomplished by MPLC over silica gel eluting with 20:10:1 toluene-dioxane-acetic acid to give 323 mg (70%) of colorless solid: mp 70-72°C; R_f 0.19 (20:10:1 toluene-dioxane-acetic acid); NMR ($CDCl_3$) δ 5.94 (m, complex, 1 H), 5.29 (m, 1 H),

5.14 (m, 1 H), 4.64 (d, J = 3.8, 1 H), 2.44 (m, 2 H), 1.84 (br, 13 H); ^{13}C NMR ($CDCl_3$) δ 161.1, 134.7, 115.9, 76.9, 65.5, 51.3, 35.2, 31.5, 30.4, 27.7, 17.8, 16.6; IR ($CDCl_3$) 2960 (s), 2880, 2860, 1640 (s), 1460, 1440, 1400, 1030, 920 cm^{-1}; mass spectrum, CI methane, M/Z (rel intensity) 222.1 (100), 221.1 (5), 206.1 (5), 178.0 (6); Anal.: ($C_{13}H_{19}NO_2$) C, H.

Thermal initiation: Allyl compound 14 was also prepared by the addition of 2 equiv of allyltri-n-butylstannane (511 mg, 1.54 mmol) and 0.15 equiv 2,2'-azobis(2-methylpropri̇onitrile) (AIBN; 21 mg, 0.116 mmol) to bromide 13 (200 mg, 0.772 mmol) in dry benzene (2 mL). The solution was degassed 15 min and heated at reflux 5 h. Removal of the benzene in vacuo and partitioning between pentane and acetonitrile gave 150 mg (88%) of the crude allyl compound.

Reaction of methyl-4-O-benzoyl-6-deoxy-6-bromo-α-D-glucopyranoside (15a) with allyltri-n-butylstannane.

Photochemical initiation: The above glucose derivative[5] (337 mg, 1.00 mmol) was placed in a 5.0 mm thin wall NMR tube, and allyltri-n-butylstannane (690 mg, 2.00 mmol), toluene (2.0 mL) and ethyl acetate (0.75 mL) were added. The atmosphere above the liquid phase was replaced with argon and, after vigorous shaking, the tube was photolysed for 18 h. The reaction was now complete by thin layer chromatography and the solvents were removed under reduced pressure to render a crude oil which was chromatographed over silica gel to give 272 mgs (91%) of product as a thick colorless oil contaminated with ca. 10% of reduced (6-debromo) material which could not be removed by chromatography over silica gel.

Thermal initiation: The same glucose derivative (3.37 g, 10.0 mmol) was placed in a 100 mL pear shaped flask and allyl-tri-n-butylstannane (6.60 g, 20.0 mmol), 20 mL of toluene, and AIBN (328 mg, 0.20 mmol) were added. The mixture was degassed for 0.5 h and subsequently heated to 80°C in an oil bath for 14 h. The solution was then concentrated and chromatographed as before to render 2.75 g (92%) of a thick colorless oil contaminated similarly to the photochemical reaction: R_f 0.42 (60% Et_2O-hexanes); 90 MHz ^{1}H NMR ($(CD_3)_2CO$) δ 8.05 (m, 2 H), 7.55 (m, 3 H), 5.70 (m, 1 H), 4.85 (m, 3 H), 4.40 (m, 2 H), 3.85 (m, 2 H), 3.50 (m, 2 H), 3.37 (s, 3 H), 2.17 (m, 2 H), 1.50 (m, 2 H); 20 MHz ^{13}C NMR ($(CD_3)_2CO$) δ 166.4, 139.1, 133.9, 130.3, 130.0, 115.1, 100.8, 76.3, 73.8, 72.7, 69.0, 55.6, 31.65, 30.1; IR (neat) 3400 (br), 2920, 1715, 1260, 900, 705 cm^{-1}; mass spectrum (EI) 322.3 (0.2), 129 (33.3), 105.1 (100), 77.1 (33.3), 74.1 (67.7).

1-Deoxy-1-thiophenyl-2,3-isopropylidene-4-(t-butyl-dimethylsilyloxy)-L-lyxose (29). To a solution of 2,3-isopropylidene-4-(t-butyldimethylsiloxy)-L-lyxose (600 mg, 1.97 mmol) in 30 mL of dichloromethane was added diphenyl disulfide (859 mg, 3.94 mmol) and tri-n-butylphosphine (0.97 mL, 3.94 mmol). The mixture was then stirred 24 h at ambient temperature at which time complete conversion was noted by TLC analysis. Water (50 mL) was added and the mixture was extracted with 3 x 50 mL of ether. The organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was chromatographed over silica gel (7% ether-hexanes) to give 678 mg (87%) of 29 as a colorless oil (ca. 4:1 mixture of α:β thiophenylglycosides), R_f 0.66, 0.51 (20% ether-hexanes), spectral data for major anomer. ^{1}H NMR ($CDCl_3$) 7.48 (m, 2 H), 7.25 (m, 3 H), 5.10 (d, 1 H, J = 3 Hz), 4.60 (d of d, 1 H, J = 3, 6 Hz), 3.90 (m, 3 H), 3.25 (m, 1 H), 1.55 (s, 3 H), 1.35 (s, 3 H), 0.80 (s, 9 H), 0.03 (s, 6 H); IR (neat) 3060, 2940, 1580, 1380, 1112, 840, 780 cm^{-1}; ^{13}C NMR ($CDCl_3$, TMS, partial) 130.6, 129.0, 127.1, 83.9, 79.1, 75.9, 69.0, 68.6, 27.7, 26.1, 25.7, 17.9, -4.63; mass spectrum (CI, isobutane) 397 (M + 1, 0.4), 287 (M-SØ, 100), 229 (15.5), 110.9 (30.6), 59 (38.8), 58.1 (79.3); Anal.: ($C_{20}H_{32}O_4SiS$) C, H.

1-Deoxy-1-allyl-2,3-isopropylidene-4-(t-butyldimethylsilyloxy)-L-lyxose. The above lyxose derivative (29) (126 mg, 0.318 mmol) was placed in a 5.0 mm thin wall NMR tube along with 600 μl of toluene. Allyltri-n-butylstannane (210 mg, 0.636 mmol) was added and the atmosphere above the solution in the tube was replaced with argon. After shaking the tube vigorously, it was photolysed with a Pyrex filter for 40 h (during which time it darkened markedly) and the crude reaction mixture was concentrated under reduced pressure. Chromatography over silica (6% ether-hexanes) gave 85 mgs (82%) of a thick colorless oil as a 92:8 mixture of α and β anomers. Physical data for the α anomer: R_f 0.68 (20% ether-hexanes); ^{1}H NMR ($CDCl_3$) 5.90 (m, 1 H), 5.15 (m, 2 H), 4.00 (m, 3 H), 3.75 (m, 2 H), 3.33 (m, 1 H), 2.35 (m, 2 H), 1.50 (s, 3 H), 1.39 (s, 3 H), 0.91 (s, 9 H), 0.10 (s, 6 H); IR (neat) 3062, 2920, 1635, 1370, 1380, 1060, 830 cm^{-1}; ^{13}C NMR ($CDCl_3$) 134.7, 116.9, 108.8, 76.9, 76.5, 74.3, 68.6, 67.6, 37.0, 28.3, 26.4, 25.8, 18.2, -4.76; mass spectrum (CI, isobutane) 328.9 (M + 1, 6.0), 312.9 (22.7), 270.9 (73.7), 254.9 (32.3), 252.9

(35.2), 212.9 (58.1), 170.9 (68.7), 59.0 (52.1); exact mass calcd for $C_{17}H_{32}SiO_4$ 313.1835 (M-Me), found 313.1835.

Reaction of trans-2-bromocyclohexanol (33) with allyltri-n-butylstannane.

Thermal initiation: A solution of 0.250 g (1.39 mmol) of bromohydrin 33, 0.925 g (2.79 mmol) of allyltri-n-butylstannane, and 0.046 g (0.28 mmol) of AIBN in 2.8 mL of toluene was degassed with nitrogen for 0.5 h and then heated at 80 °C (oil bath) for 8 h under nitrogen. VPC analysis revealed complete consumption of the starting bromohydrin. The mixture was diluted with 10 mL of CH_3CN and 1 mL of water, 1 g of KF was added, and the mixture was stirred at ambient temperature overnight; TLC analysis showed no tri-n-butyltinbromide remaining. The mixture was flushed through a 4" x ½" plug of adsorption alumina (Fisher, 80-200 mesh) with the aid of ether, concentrated, and chromatographed over silica gel using a gradient of 0-25% THF-hexanes to give 0.144 g (74%) of 2-allylcyclohexanol as a mixture of cis and trans isomers. VPC analysis after completion of reaction, but prior to workup, showed a cis-trans ratio of 1:3.7.

Photochemical initiation: A solution of 0.358 g (2.0 mmol) of bromohydrin 33 and 1.32 g (4.0 mmol) of allyltri-n-butylstannane in 4.0 mL of toluene was placed in a 10 mL screw top Pyrex test tube and degassed for 0.5 h with argon. The tube was then sealed and irradiated until reaction was complete by VPC analysis (26 h).

The mixture was transferred to a 25 mL flask, and 10 mL of CH_3CN, 1 mL of H_2O, and 1.5 g of KF were added, and the resulting mixture was stirred overnight. Filtration through alumina, concentration, and chromatographic isolation as described above gave 0.208 g (74%) of 2-allylcyclohexanol as a mixture of cis and trans isomers. VPC analysis of the crude reaction product prior to workup and chromatography revealed a cis-trans ratio of 1:4.1.

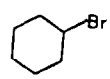
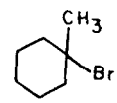
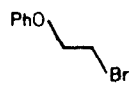
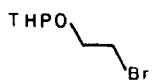
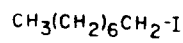
Acknowledgement: Support of this research by the National Science Foundation is gratefully acknowledged.

References and Notes:

1. For a preliminary account of some of the results described herein, note Keck, G.E. and Yates, J.B. J. Am. Chem. Soc. **1982**, 104, 5829.
2. For a recent overview of free radical reactions in organic synthesis, note Hart, D.J. Science (Washington, D.C.), **1984**, 223, 883.
3. For substrates in which X is a thioacyl derivative, X is not in fact the same on both sides of equation (1).
4. For recent leading references on the preparation of such materials, note:
   a. Nicolaou, K.C. Tetrahedron **1981**, 37, 4097.
   b. Dowle, M.D. and Davies, D.I. Chem. Soc. Rev. **1979**, 171.
   c. Hirama, M.; Iwashita, M.; Yamakazi, Y. and Itô, S. Tetrahedron Lett. **1984**, 25, 4963.
5. Hanessian, S. and Plessas, N. J. Org. Chem. **1969**, 34, 1035.
6. For a recent review of such reactions note Barton, D.M.R. and Motherwell, W.B. Pure Appl. Chem. **1981**, 53, 1081.
7. For a preliminary account and an unusual "two-electron" chain process using such thiophenyl glycosides and allylstannanes, note Keck, G.E.; Enholm, E.J. and Kachensky, D.F. Tetrahedron Lett. **1984**, 25, 1867.
8. Powell, D.W. and Vedejs, E. J. Am. Chem. Soc. **1982**, 104, 2046.
9. Keck, G.E. and Yates, J.B. J. Organomet. Chem. **1983**, 248, C21.
10. Webb, R.R. and Danishefsky, S. Tetrahedron Lett. **1983**, 24, 1357.
11. Barton, D.H.R.; Hartwig, W. and Motherwell, W.B. J. Chem. Soc. Chem. Comm. **1982**, 447.
12. Chamberlain, A.R.; Dezube, M.; Dussalt, P. and McMills, M. J. Am. Chem. Soc. **1983**, 105, 5819.
13. Houk, K.; Caramella, R.; Ronda, N. and Paddon-Row, M. J. Am. Chem. Soc. **1981**, 103, 2483.

14. Keck, G.E. and Yates, J.B. J. Org. Chem. **1982**, 47, 3590.
15. Keck, G.E.; Kachensky, D.F. and Enholm, E.J. J. Org. Chem. **1984**, 49, 1462.
16. (a) Keck, G.E. and Kachensky, D.F.; unpublished results.
(b) Portions of this work have been described: Kachensky, D.F. and Keck, G.E.; Paper #165, Philadelphia ACS Meeting, 1984.
17. Seyferth, D. and Weiner, M.A. J. Org. Chem, **1961**, 26, 4797.

Table I. VPC Yields for Free Radical Allylation and Methallylation of Simple Alkyl Halides[a,b]

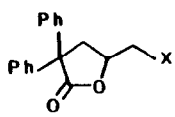
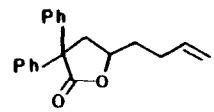
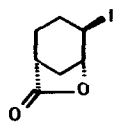
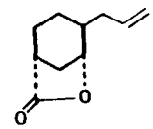
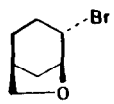
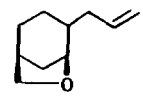
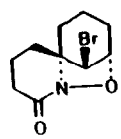
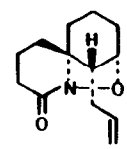
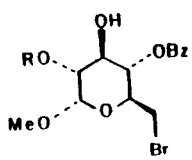
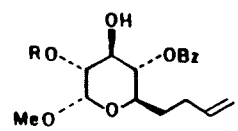
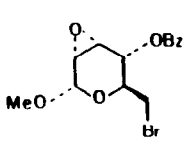
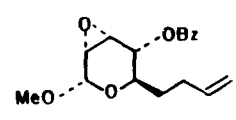
Substrate		Yield	Substrate		Yield
1		88 (72)	4		90
2		57	5		65 (89)
3		98 (89)	6		68

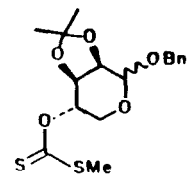
(a) All products were as given in equation 1, i.e. with allyl or methallyl replacing halogen in each case.

(b) Yields obtained with methallyltri-n-butylstannane are given in parentheses.

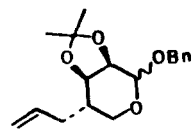
Table II: Isolated Yields for Free Radical

Allylation and Methallylation in More Complex Systems

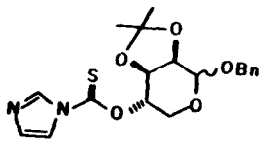
	Substrate	Method[a]	Product[b]	Yield[c]
				
7a	X=Br	Δ hν	8	88 (97) 82
7b	X=SePh	Δ hν	8	79 75
7c	X=SPh	Δ hν	8	-- --
9		Δ hν	10 	65 81
11		hν	12 	66
13		Δ hν	14 	88 70
				
15a		R=H Δ hν	16a	92 91
15b		R=Ts Δ hν	16b 	74 60
17		Δ	18	76

19a 

Δ
hν

20 

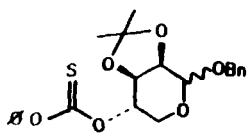
13
62

19b 

Δ
hν

20

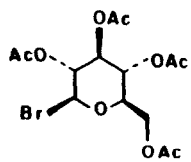
27
55

19c 

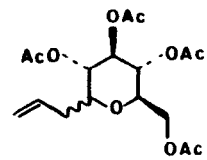
hν

20

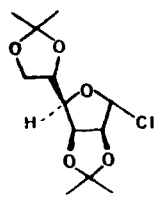
80

21 

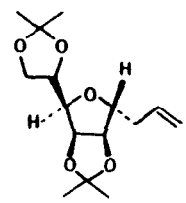
Δ
hν

22 

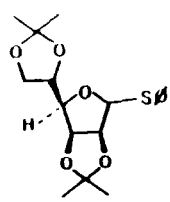
64
52

23 

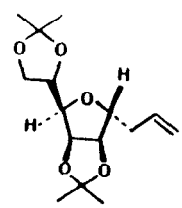
Δ
hν

24 

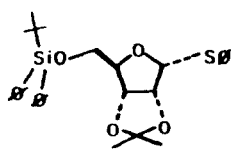
79
68

25 

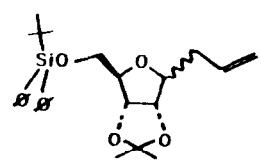
hν

26 

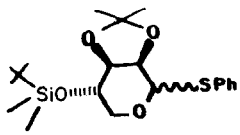
91 (72)

27 

hν

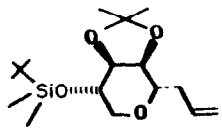
28 

76 (86)



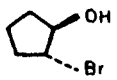
29

hν



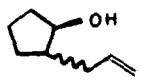
30

82 (87)



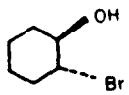
31

Δ
hν



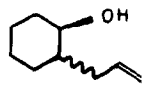
32

71
67



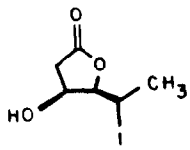
33

Δ
hν



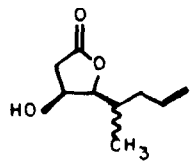
34

74
74



35

hν



36

68

(a) Here Δ refers to reactions conducted with AIBN as initiator at 80° in benzene or toluene, using 2.0 equivalents of stannane and concentrations of ca. 0.5 M in substrate, while hν refers to photochemically initiated reactions conducted at ambient temperature, using the same concentrations and stoichiometry.

(b) Only structures for allylated products are shown. Reactions with methallyltri-n-butylstannane (see (c) below) yield analogous products with the allyl unit replaced by a methallyl unit.

(c) Values in parentheses refer to results obtained with methallyltri-n-butylstannane.