Tributylstannane-Mediated Cyclization of Thionocarboxylic Acid Derivatives

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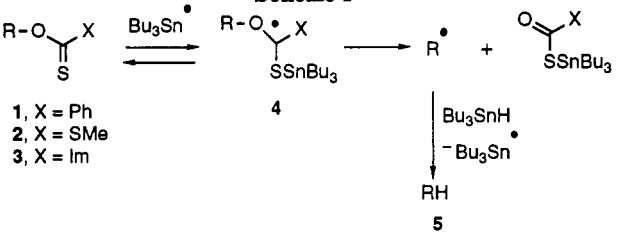
Cyclization reactions of various thionoesters and thioamides involving the addition of tri-*n*-butylstannyl radical to a thiocarbonyl group and intramolecular addition of the resulting radical to a carbon–carbon multiple bond was studied. Dithiocarbonate and (imidazolyl)thiocarbonyl derivatives of homoallylic alcohols gave α-substituted γ-thionobutyrolactones. The reaction is highly dependent on the substitution pattern on the double bond, a high yield of cyclic products being obtained only when the double bond is activated and unhindered. (*Z*)-4-Phenylbut-3-enyl thionobenzoate afforded 4,5-dihydro-2-phenyl-3-benzylfuran in low yield. In reactions involving a thioamide group, good yields of cyclic products were obtained only from compounds in which the electron density on the nitrogen atom is decreased by an electron attracting group. Cyclization of 1-((*E*)-4-phenylbut-3-en-1-yl)-5-thioxopyrrolidin-2-one (**23**) afforded 1-aza-4-benzylbicyclo[3.3.0]oct-4-en-8-one (**33**).

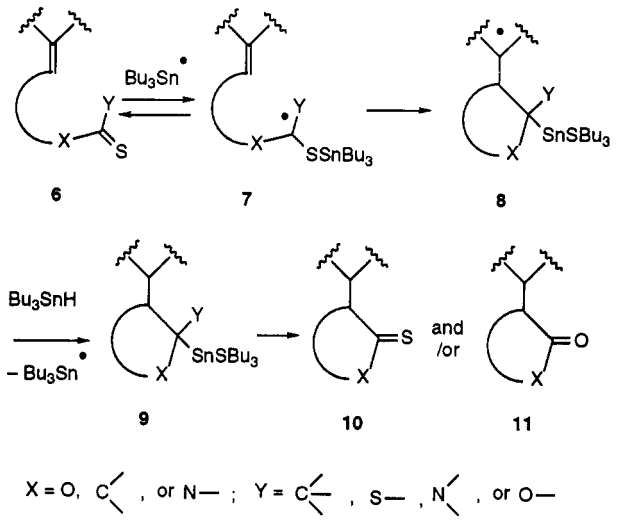
Barton and McCombie demonstrated that *O*-alkyl thiobenzoates **1**, *O*-alkyl *S*-methyl dithiocarbonates **2**, and (alkoxy(thiocarbonyl))imidazolides **3** are reduced to deoxy compounds **5** by trialkylstannanes according to a mechanism which involves the reversible attack of the thiono sulfur atom by a stannyl radical (Scheme I).[1,2] This and similar reactions are extensively used for the reduction of alcohols under mild nonpolar conditions.[3-5] In a preliminary communication[6] we have shown that the dithiocarbonates and imidazolide derivatives of 4-phenyl-3-butenol afford, under the Barton and McCombie reaction conditions, α-benzyl-γ-buthyrothionolactone.[7] Thus radical intermediates of type **4**, possessing a radical trap in a suitable position on the tether R, may undergo ring closure rather than degradation. On the grounds of this observation we investigated the potential value of the free radical reaction of tri-*n*-butylstannane with various thiocarbonyl compounds of the general structure **6** for the synthesis of cyclic compounds of type **10** and/or **11** (Scheme II). In this paper we give a full account of the synthetic and mechanistic aspects of our study.

A series of reactions of various thiocarbonyl derivatives with *n*-Bu_3SnH (stoichiometric amount) and AIBN (catalytic amount), in boiling benzene or toluene, are summarized in Table I. Cyclization of the *O*-alkenyl dithiocarbonate bearing a double bond activated by a phenyl group (entries 1 and 2) results in the formation of the thionolactone in good yield. When an unactivated double bond is involved the yield drops down to about 50% (entry 3), and when the double bond is sterically hindered cyclization is retarded and only traces of thionolactone were detected (entry 4). Cyclization of dithiocarbonates is thus highly dependent on the reactivity of the double bond and on the steric accessibility to it. Three hypothetical mechanisms for cyclization of dithiocarbonates derived from but-3-enyl alcohols are shown in Scheme III. According to reaction path a and b a *n*-$Bu_3Sn^\bullet$ adds reversibly to the thiono sulfur atom of the dithiocarbonate **36** as in

Scheme I



Scheme II



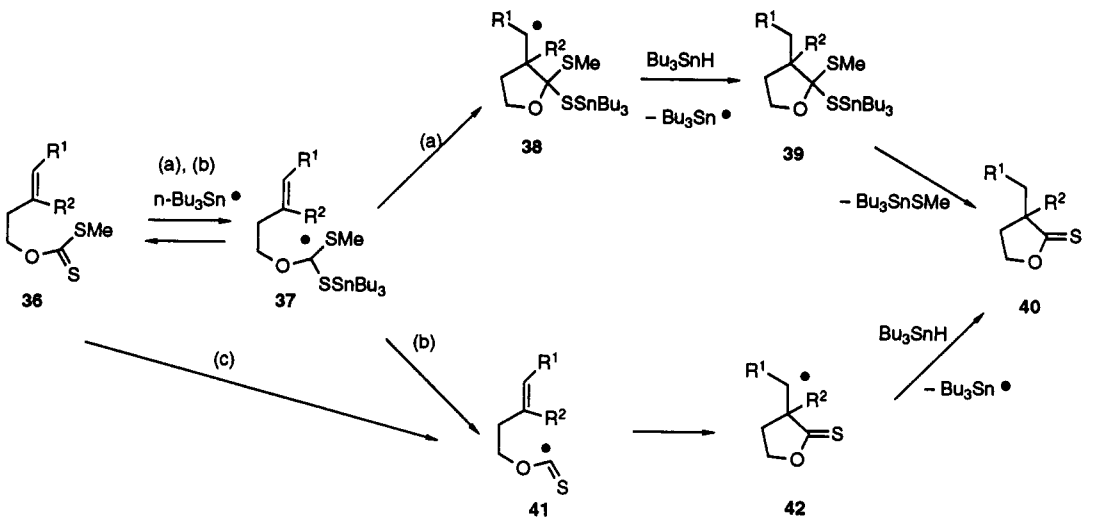
the Barton–McCombie deoxygenation reaction.[1,2] The adduct radical **37** may add to the double bond to give the cyclic radical **38** (path a) which then abstracts an H atom to give the ortho thionolactone **39**. On elimination of methyl tributylstannyl sulfide, the thionolactone **40** is produced. Alternatively (path b), methyl tributylstannyl sulfide may be eliminated from **37** to give the butenyloxy thiocarbonyl radical **41**[2] which, after cyclization to radical **42**, is converted into the thionolactone **40** through H atom transfer (path b). Reaction according to path c in which radical **41** is generated through methylthio group abstraction from **36** by *n*-$Bu_3Sn^\bullet$ was excluded on the grounds of previous studies.[1,2,8]

We recently reported[9,10] that the *n*-Bu_3SnH/AIBN-induced cyclization of *Se*-phenyl selenocarbonates derived

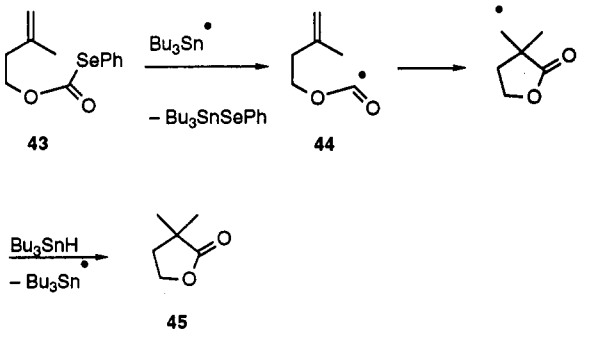
(1) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.
(2) Barton, D. H. R.; Crich, D.; Löbberding, A.; Zard, S. Z. *Tetrahedron* **1986**, *42*, 2329.
(3) Hartwig, W. *Tetrahedron* **1981**, *39*, 2609.
(4) Robins, M. J.; Wilson, J. S.; Hansske, F. *J. Am. Chem. Soc.* **1983**, *105*, 4059.
(5) Prisbe, E. J.; Martin, J. C. *Synth. Commun.* **1985**, *15*, 401.
(6) Bachi, M.; Bosch, E. *J. Org. Chem.* **1989**, *54*, 1234.
(7) See also: (a) Iwasa, S.; Yamamoto, M.; Kohomoto, S.; Yamada, K. *J. Org. Chem.* **1991**, *56*, 2849. (b) Iwasa, S.; Yamamoto, M.; Kohmoto, S.; Yamada, K. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1173.
(8) Bachi, M. D.; Bosch, E. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1517.
(9) Bachi, M. D.; Bosch, E. *Heterocycles* **1989**, *28*, 579.
(10) Bachi, M. D.; Bosch, E. *J. Org. Chem.* **1992**, *57*, 4696.

0022-3263/92/1957-6803$03.00/0

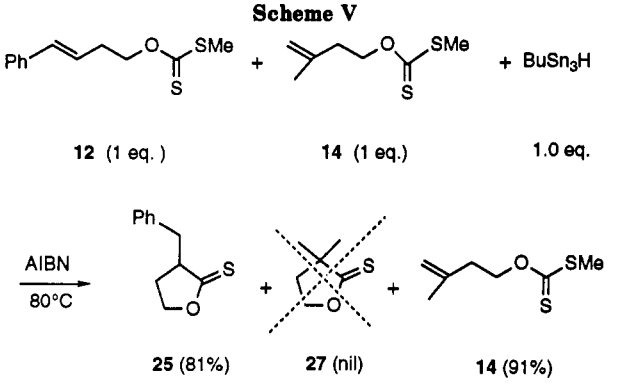
Scheme III



Scheme IV



Scheme V

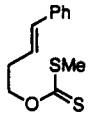
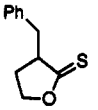
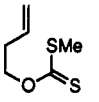
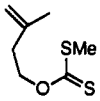
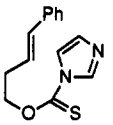
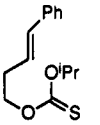
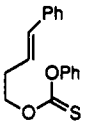
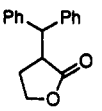
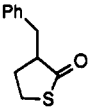
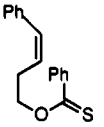
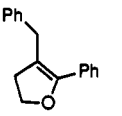


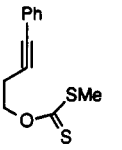
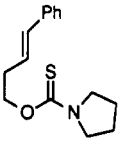
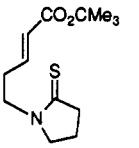
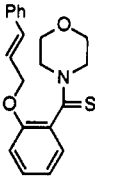
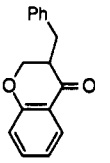
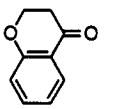
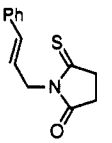
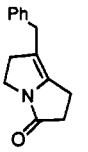
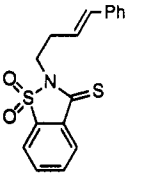
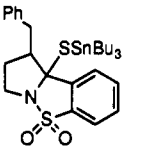
from alk-3-enyl alcohols affords γ-lactones in excellent yields even when their double bond was both sterically hindered and unactivated.[9,10] Indeed, the phenyl selenocarbonate **43** affords 3,3′-dimethylbutyrolactone (**45**) in quantitative yield. This reaction involves the 5-exo cyclization of the (alkenyloxy)carbonyl radical **44** (Scheme IV).[10] The fact that the cyclization reaction of *O*-alk-3-enyl dithiocarbonates was found to be much more dependent on the substitution pattern of the double bond than the analogous cyclization of *O*-alk-3-enyl (phenylseleno) carbonates implies the participation of different types of intermediates at the ring-forming step. Reasonably, the ring closure of dithiocarbonates involves trihetero-substituted free radical **37**, and not an oxythiocarbonyl radicals **41**. The steric interaction produced at the transition state for addition of the bulky tertiary radical onto the substituted double bond in **37**, as well as the cumulative stabilizing effects of the three hetero substituents, greatly diminish the rate of cyclization as compared to that of the oxycarbonyl radical in **44**. Reasonably this difference would not be observed if the oxythiocarbonyl radical **41** was involved. NMR and UV analyses of reaction mixtures indicate that thionolactones **40** are formed in the reaction mixtures and not through hydrolysis on silica gel as reported[8] for the formation of thiololactones **29** from intermediate **49** (vide infra, Scheme VI). The fast elimination of methyl tributylstannyl sulfide avoids other secondary reactions of ortho lactone intermediates **39** and allows the production of thionolactones **40** in good yields. Additional support for reaction according to path a of Scheme III is provided by the following experiment.

A mixture of 1 equiv each of the *S*-methyl dithiocarbonates **12** and **14** were reacted with 1 equiv of *n*-Bu_3SnH in boiling benzene under standard conditions. After 20 min NMR analysis of the crude product indicated complete consumption of *n*-Bu_3SnH and **12** while dithiocarbonate **14** remained intact. Flash chromatography of the residue yielded the thionolactone **25** (81%) and unreacted dithiocarbonate **14** (91%) (Scheme V). Both compounds **12** and **14** are derived from primary alcohols, and while differing in the substitution pattern on the double bond, their structures in the proximity of the dithiocarbonyl group are identical. When reacted individually with 1 equiv of *n*-Bu_3SnH, both compounds were quantitatively consumed in a rapid reaction (Table I note *c*, entries 2 and 4). It is thus reasonable to assume that if an irreversible homolytic reaction as in path b or c of Scheme III had followed, then **12** and **14** would generate the respective alkoxy(thiocarbonyl) radicals of type **41** at about the same rate. Thus, irrespective of the fate of these radicals, about 50% each of the dithiocarbonate **12** and **14** would have been consumed in the reaction described in Scheme V, and no more than 50% of **12** and of **14** would be recovered. The selective reaction of only one of the two dithiocarbonates implies a reversible addition of the tri-*n*-butyltin radical to the thiocarbonyl group to give trihetero atom-substituted radicals of type **37**. The unhindered and activated double bond present in **12** facilitates cyclization leading ultimately to thionolactone **25** while ring closure onto the hindered unactivated double bond of **14** is inhibited. Thus, an apparent selective reaction of **12** in the presence of **14** is observed.

This experiment gives additional support to the method we used for proving the mechanism of the Barton–McCombie radical deoxygenation reaction which is based on product analysis of the reaction described in Scheme VI.[8] The use of the *S*-(4-alkenyl) dithiocarbonate **46** as

Table I. Cyclization of *O*-Thiocarbonyl Compounds 6 Mediated by *n*-BuSnH/AIBN

	thiocarbonyl derivatives	procedure[a]	product (yield)[b]
(1)	 **12**	Ac	 **25** (70%)
(2)	**12**	Bc	**25** (77%)
(3)	 **13**	Bc	 **26** (51%)
(4)	 **14**	Bc	 **27**(<2%)
(5)	 **15**	Ac	**25**(70%)
(6)	 **16**	A, Bc	**25**(traces)
(7)	 **17**	Ac	 **28**(47%)  **29**(13%) **25**(8%)
(8)		Ec	**28**(49%) **29**(37%) **25**(nil)
(9)	 **18**	Cc	 **30**(30%)

	thiocarbonyl derivatives	procedure[a]	product (yield)[b]
(10)	 **19**	Dc	**25**(49%)
(11)	 **20**	A	no reaction
(12)	 **21**	E	no reaction
(13)	**21**	F	decomposition
(14)	 **22**	A	no reaction
(15)	**22**	Gc	 **31**(10%)  **32**(32%)
(16)	 **23**	E, F	 **33**(54–64%)
(17)	 **24**	E, F	 **34**(54–60%)

[a] Procedures: (A) Solutions of Bu_3SnH (1.15 equiv) and AIBN (0.15 equiv) in benzene are added (ca. 2 h) to a boiling solution of thiono derivative in benzene. (B) A solution of thiono derivative (1 equiv, 0.02 M), Bu_3SnH (1.15 equiv), and AIBN (0.15 equiv) are boiled in benzene. (C) As in A but in boiling toluene. (D) As in A but with 2.3 equiv of Bu_3SnH. (E) As in B but in boiling toluene. (F) As in B but in boiling xylene. (G) As in A but in boiling xylene. [b] Yield of isolated product. [c] Reactions were continued until all starting material was consumed (TLC).

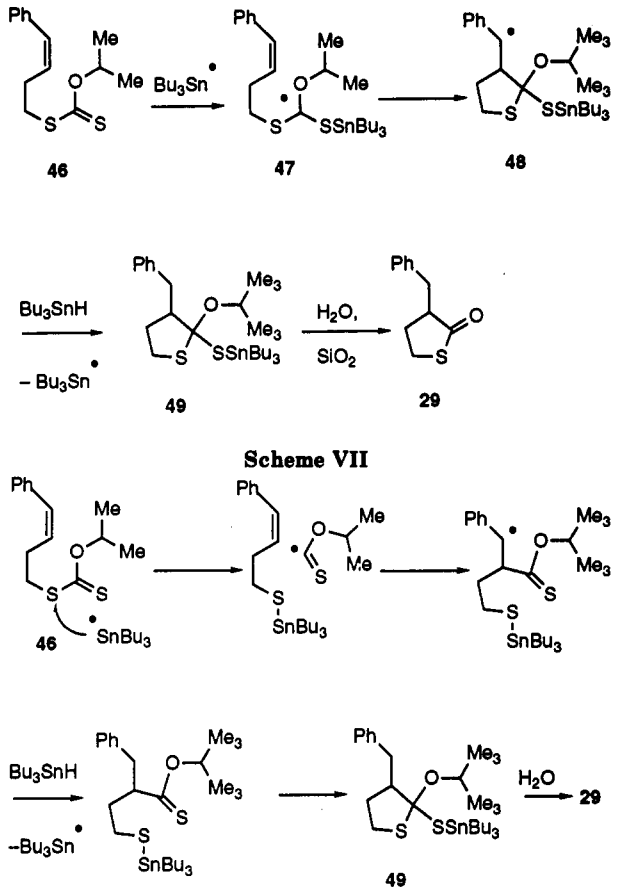
a mechanistic probe was challenged by Crich[11] who claimed that the formation of thiololactone **29** does not necessarily involve intermediates **47** and **48** as suggested by us as a proof for stannyl radical addition to the thiocarbonyl group. He proposed the alternative mechanism described in Scheme VII which involves stannyl radical attack on the thiolo sulfur atom, followed by recombination of the resultant two fragments, and a nonradical cyclization to the ortholactone **49**.[11] The validity of Crich's mechanism, which has no parallel in the literature, has been questioned on theoretical grounds.[12] The experiment described above on the competitive reaction of the *S*-methyl dithiocarbonates **12** and **14** with *n*-Bu_3SnH disproves it on experimental grounds.

Cyclization of [(alkenyloxy)(thiocarbonyl)]imidazolides **15** (entry 5) is similar to that of the corresponding di-

(11) Crich, D. *Tetrahedron Lett.* **1988**, *29*, 5805.

(12) Minisci, F. In *Sulfur-Centered Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K., Eds.; Plenum Press: New York, 1990; p 303.

Scheme VI



Scheme VII

thiocarbonate **12**. Reaction of isopropyl thionocarbonate **16** with *n*-Bu_3SnH (entry 6) resulted in the full consumption of the thionocarbonate, but only a trace of thionolactone **25** was isolated. NMR examination of the crude residue showed that the double bond was no longer present, which indicates that there was cyclization. It seems that due to the failure of the tetrahedral intermediate of type **9** (X = O, Y = ^{i}PrO) to yield a thionolactone of type **10** (X = O) through a fast elimination of *n*-Bu_3SnO^iPr, other (not investigated) secondary reactions predominate.

An interesting rearrangement was observed in the reaction of phenyl thionocarbonate **17** under standard conditions in benzene (entry 7).[13] The "normal" reaction product, namely the thionolactone **25**, was obtained in only 8% yield along with the thiololactone **29** (13%). The major product was the diphenylmethyl lactone **28** (47%). In order to check if the second phenyl group in **28** derives from homolytic substitution on benzene, the reaction was repeated in toluene. In this experiment (entry 8) the diphenylmethyl lactone **28** was also found to be the major reaction product thus proving that the two phenyl groups in **28** originate from the thionocarbonate **17**. We suggest that the initial reversible attack of the tri-*n*-butyltin radical on the thionocarbonyl group is followed by cyclization of the adduct radical **50** as observed for thiono derivatives **12** and **15** (Scheme VIII). The cyclized radical **51** may then undergo either one of two competing processes. The major process, under our reaction conditions, involves an intramolecular radical addition onto the aromatic ring of the phenoxy group. The cyclohexadienyl radical **52** so formed undergoes rearomatization and carbonyl formation with concomitant elimination of a (tri-*n*-butylstannyl)thiyl radical and formation of the diphenyl lactone **28**. The minor process, under our reaction conditions, involves a "regular" reduction of compound **51** by *n*-Bu_3SnH to give the ortho lactone **53** which upon spontaneous elimination of (phenoxy)tributyltin affords the thionolactone **25**. Thermal rearrangement results in the formation of the thiololactone **29**. The extent of this rearrangement appears to be a function of the reaction time and temperature and was complete in the experiment performed at higher temperature (entry 8).[14] When phenyl thionocarbonate derivatives are used for the purpose of reducing alcohols with *n*-Bu_3SnH[4] double bonds which can act as intramolecular radical trap and initiate a set of transformations of the type described in Scheme VIII should be avoided, otherwise rearrangement of this type may interfere with the desired straight reduction.[15]

O-Alkenyl thiobenzoate **18** affrded the dihydrofuran **30**. Reasonably, the mechanism of this reaction involves cyclization of adduct radical **54** to benzylic radical **55**. Hydrogen atom transfer to **55** and elimination of *n*-Bu_3SnSH from **56** (probably through an E_1 mechanism) results in the dihydrofuran **30** (Table I, entry 9, and Scheme IX).

A secondary process was observed also in the reaction of the dithiocarbonate **19** (Table I, entry 10, and Scheme X).[16] Consumption of the starting material required a little more than 2 equiv of *n*-Bu_3SnH, and the reaction product was identified as the α-benzyl-γ-thionolactone **25**. It seems that the α-benzylidene-γ-thionolactone **58** was initially formed through the cyclization of the acetylenic compound and subsequent elimination of methyl tributylstannyl sulfide from the intermediate ortho lactone **57**. However due to conjugation with the benzylidene group, the thiocarbonyl group in **58** reacts with tributylstannyl radicals at a higher rate than the thiocarbonate **19** and is therefore reduced to the tributylstannyl thioenolate **59**. Hydrolysis on silica gel affords the thionolactone **25**. This sequence of events was coorborated by noting that a sample of benzylidene thionolactone **58**, prepared by treatment of α-benzylidene γ-lactone with Lawesson's reagent,[17] was rapidly reduced to α-benzyl γ-thionolactone **25** by *n*-Bu_3SnH under standard conditions. A similar transformation was observed by Angoh and Clive on treatment of an acetylenic thiocarbonylimidazolide with Ph_3SnH/AIBN.[18] It was recently reported that *n*-Bu_3SnH/Et_3B-mediated cyclization of dithiocarbonate **19** affords the benzylidenethionolactone **58** when performed (and quenched) at −78 °C.[19]

The potential value of thioamides as substrates in *n*-Bu_3SnH/AIBN-induced cyclizations was tested using the thiocarbamate **20**, the thiopyrrolidone **21**, the salicylthioamide **22**, the monothiosuccinimide **23**, and the thiosaccharide **24** (Table I, entries 11–17). It was found that, under the standard conditions employed for the cyclization

(13) This rearrangement was reported at the NATO Advanced Research Workshop on Free Radicals in Synthesis and Biology, Bardolino (VR), Italy, May 1988. Bachi, M. D.; Bosch, E.; Denenmark, D.; Girsh, D. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer Academic Publishers: Boston, 1989; p 125. s.a. ref 6.

(14) It appears that an unidentified component of the reaction mixture catalyses the rearrangement of **25** as there was no evidence for it in any of the other reactions (entries 1–6).

(15) Gruszecha-Kowalik, E.; Zalkow, L. H. *J. Org. Chem.* **1990**, *55*, 3398.

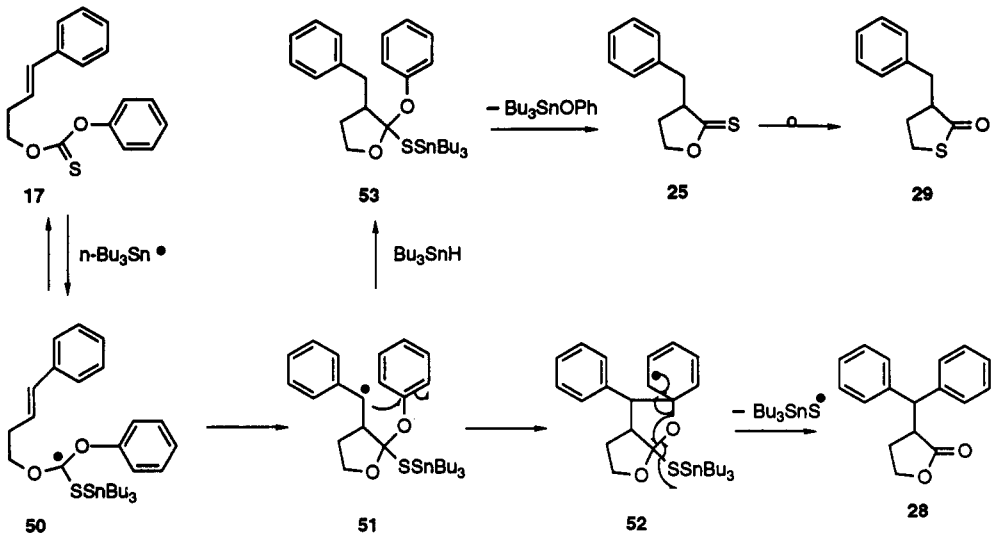
(16) For preliminary report see: Bachi, M. D.; Bosch, E. *Tetrahedron Lett.* **1986**, *27*, 641.

(17) Scheibye, S.; Kristensen, J.; Lawesson, S.-O. *Tetrahedron* **1979**, *35*, 1339.

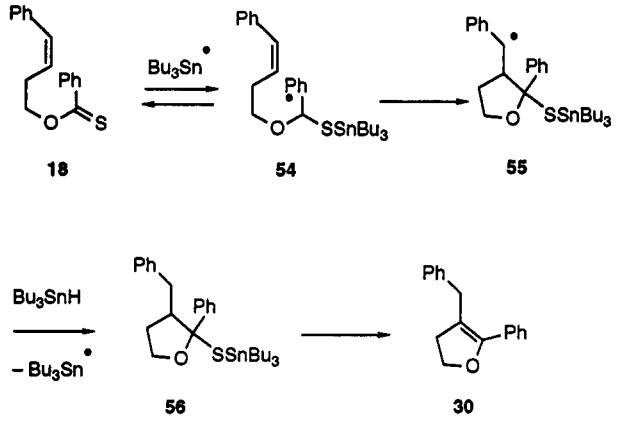
(18) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 980.

(19) Nozaki, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2578.

Scheme VIII



Scheme IX



of the thiocarbonates described in Table I, the thioamides **20**, **21**, and **22** do not react, and starting materials were recovered in very high yield (entries 11–14). A small amount of cyclization products **31** and **32** were obtained from the salicylthioamide **22** when the reaction was performed under more drastic conditions (Table I, entry 15, and Scheme XI). It seems that the *n*-BuSnS group in the cyclization product **60** is abstracted by *n*-BuSn• to give intermediate radical **61** which, through β-elimination of a benzyl radical, gives the enamine **62**. Compounds **60** and **62** are hydrolyzed during chromatography on silica gel to give respectively the chromanones **31** and **32**. The inert nature of thioamides **20–22** toward tributylstannyl radicals is attributed to the stabilizing power of the nitrogen atom. Although adduct radicals of type **7** (X or Y = N) are reversibly produced under the reaction conditions, they are not sufficiently reactive to maintain a viable chain reaction through addition to the double bond.

The stabilizing power of the nitrogen atom can be reduced by electron-withdrawing substituents.[20] Thus good yields of cyclization products were obtained in the reaction of *n*-Bu_3SnH/AIBN with the monothiosuccinimide **23** (Table I, entry 16, and Scheme XII) and with the thiosaccharide **24** (Table I, entry 17, and Scheme XIII). Thus, treatment of the monothiosuccinimide **23** with *n*-Bu_3SnH/AIBN in boiling toluene or xylene afforded the azabicyclooctenone **33**. Evidently compound **33** is obtained in a E_1 elimination of "*n*-Bu_3SnSH" from the product of free radical cyclization **63** (not isolated). A similar reaction of the thiosaccharide **24** afforded the polycyclic product **34**. This compound is thermally stable but eliminates "*n*-Bu_3SnSH" upon treatment with TFA to give **35** (quantitative yield).

We conclude that various thiocarbonyl compounds of type **6** undergo *n*-Bu_3SnH/AIBN-mediated cyclization to thiocarbonyl compounds **10**. However high yields of cyclic products are obtained only when the intramolecular free radical addition is supported by activation of the double bond (Table I, entries 1, 2, and 5), introduction of geminal substituents,[7a] or formation of fused systems (Table I, entries 16 and 17).

Experimental Section

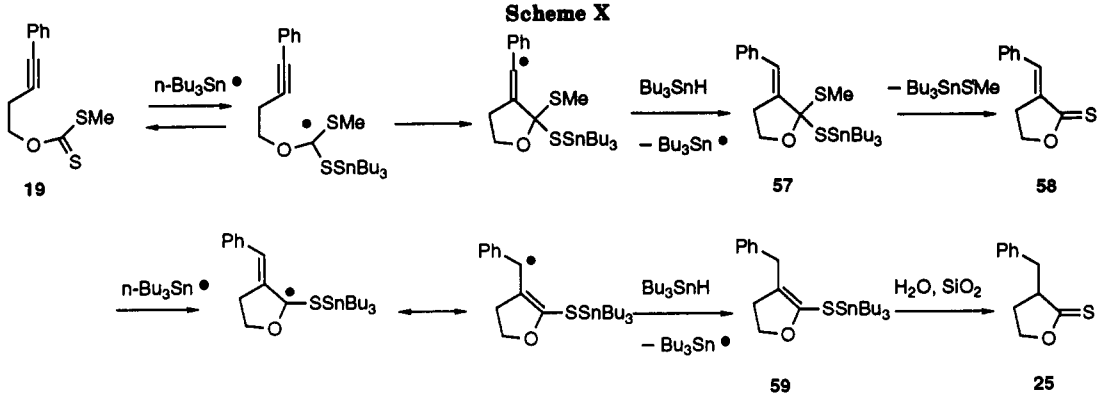
General Procedures. Unless otherwise stated all solvents were dried by conventional methods, and the reactions were performed in flame- or oven-dried glassware under an atmosphere of argon. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F-254). "Standard workup" refers to partition of the reaction mixture (1 mmol) between EtOAc (70 mL) and water (30 mL), washing the organic layer with cold dilute HCl (30 mL), saturated aqueous $NaHCO_3$ solution (30 mL), brine (30 mL), and water (30 mL), drying over $MgSO_4$, and evaporation of the solvent. Flash chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh). Preparative TLC was performed on glass plates precoated with silica gel (Merck, Kieselgel 60 F-254). Unless otherwise stated ^1H NMR spectra were recorded in $CDCl_3$ on a 270-MHz spectrometer, and their signal assignments were supported by appropriate decoupling.

General Procedure for the Preparation of *S*-Methyl Dithiocarbonates, 12, 13, and 14. A mixture of a homoallylic alcohol (2.0 mmol) and sodium hydride (3.0 mmol) in THF (20 mL) was boiled for 1 h. The solution was cooled, CS_2 (1.0 mL) was added, and the solution was boiled for 30 min. After cooling, methyl iodide (1.0 mL) was added and the solution boiled for a further 30 min. The mixture was then cooled, diluted with EtOAc, and worked up by standard conditions. Flash chromatography of the residue yielded the *S*-methyl dithiocarbonate of the corresponding homoallylic alcohol which was distilled before use.

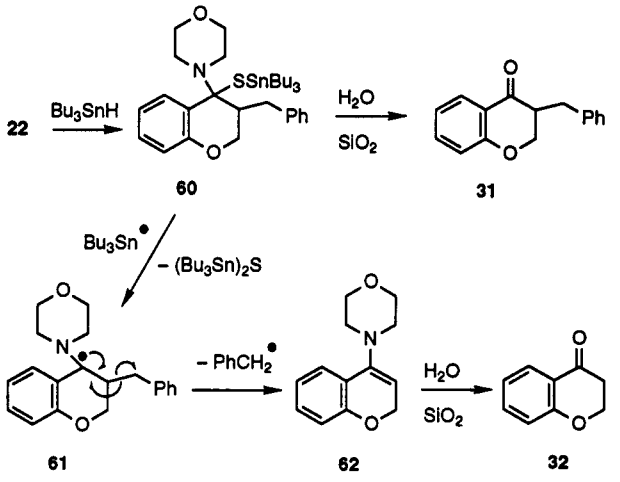
***O*-((*E*)-4-Phenylbut-3-en-1-yl) *S*-methyl dithiocarbonate (12)**: yield 90% from (*Z*)-4-phenylbut-3-en-1-ol; IR (film) 3027, 2948, 1220s, 1180s, 1065s, 965, 744, 693, and 666 cm^{-1}; ^1H NMR δ 2.56 (s, 3 H, SCH_3), 2.72 (apparent dq, J = 6.8, 1.3 Hz, 2 H, $CH{=}CHCH_2CH_2$), 4.71 (t, J = 6.7 Hz, 2 H, CH_2CH_2O), 6.20 (dt, J = 15.9 and 7.0 Hz, 1 H, $CH{=}CHCH_2$), 6.52 (d, J = 15.9 Hz, 1 H, $PhCH{=}CH$), 7.19–7.43 (m, 5 H, ArH); UV λ_{max} (EtOH) 252 (17500) and 276 nm (12000); MS *m/e* 131 (23), 130 ($M - C_2H_4OS_2$, 100), 129 (36), 115 (27), 91 (62). Anal. Calcd for $C_{12}H_{14}OS_2$: C, 60.47; H, 5.92; S, 26.90. Found: C, 60.70; H, 5.86; S, 26.81.

(20) Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *J. Org. Chem.* **1985**, *50*, 5620.

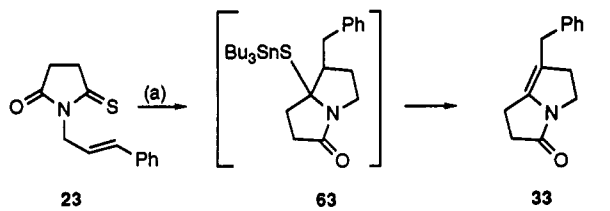
Scheme X



Scheme XI

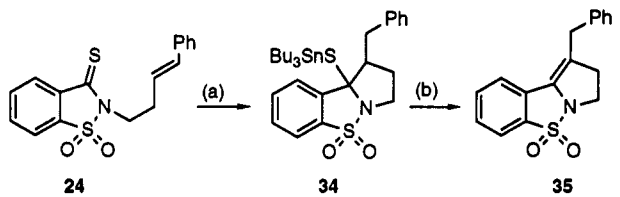


Scheme XII[a]



[a] (a) *n*-Bu_3SnH, AIBN.

Scheme XIII[a]



[a] (a) *n*-Bu_3SnH, AIBN; (b) TFA.

***O*-(But-3-en-1-yl) *S*-methyl dithiocarbonate (13)**: yield 98% from but-3-en-1-ol; distilled at 83 °C (11 mmHg); IR (film) 3081, 2984, 2951, 2921, 1643, 1426, 1218 vs, 1068 vs, 920 cm^{-1}; ^1H NMR δ 2.55 (s, 3 H, SMe), 2.53–2.60 (m, 2 H), 4.64 (t, J = 6.7 Hz, 2 H, CH_2O), 5.10–5.20 (m, 2 H, C=CH_2), 5.75–5.90 (m, 1 H, CH_2=CH). Anal. Calcd for $C_6H_{10}OS_2$: C, 44.44; H, 6.22. Found: C, 44.09; H, 6.12.

***O*-(3-Methylbut-3-en-1-yl) *S*-methyl dithiocarbonate (14)**: yield 98% from 3-methylbut-3-en-1-ol; IR (film) 3073, 2970, 2921, 1652, 1448, 1424, 1220vs, 1061 cm^{-1}; ^1H NMR δ 1.79 (br s, 3 H, CCH_3), 2.52 (t, J = 6.8 Hz, 2 H, CCH_2CH_2O), 2.55 (s, 3 H, SCH_3), 4.71 (t, J = 6.8 Hz, CH_2CH_2O), 4.79 (br s, 1 H), 4.85 (br s, 1 H); UV λ_{max} (CH_2Cl_2) 280 nm (10 500). Anal. Calcd for $C_7H_{12}OS_2$: C, 47.72; H, 6.87; S, 36.33. Found: C, 46.62; H, 6.67; S, 36.59.

[[((*E*)-4-Phenylbut-3-en-1-yl)oxy](thiocarbonyl)]-imidazolide (15).[21] (Thiocarbonyl)diimidazole (514 mg, 2.9 mmol) was added to a solution of (*E*)-4-phenylbut-3-en-1-ol (290 mg, 1.96 mmol) and 4-(dimethylamino)pyridine (5 mg) in 1,2-dichloroethane (15 mL). The solution was boiled for 1 h and the solvent evaporated. Filtration of the crude product through a short column of silica gel (hexane/EtOAc, 3:1) gave 15 (451 mg, 89%) as a pale yellow oil which crystallized on cooling: mp 54–55 °C; IR (film) 3027, 2959, 1467s, 1368s, 1328s, 1286s, 1232s, 1096s, 993s, 968sh, 744, and 657 cm^{-1}; ^1H NMR (80 MHz) δ 2.67 (apparent q, J = 6.7 Hz, 2 H, $CHCH_2CH_2O$), 4.06 (t, J = 7.0 Hz, 2 H, CH_2CH_2O), 6.00 (dt, J = 6.6 and 15.9 Hz, 1 H, CH=$CHCH_2$), 6.44 (d, J = 15.9 Hz, 1 H, PhCH), 6.93 (br s, 1 H), 7.06 (br s, 1 H), 7.16–7.36 (m, 5 H), 7.49 (br s, 1 H); UV λ_{max} (EtOH) 253 (27 000), 282 (infl), 293 nm (infl). Anal. Calcd for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84. Found: C, 65.10; H, 5.77; N, 10.80.

***O*-(*E*)-4-Phenylbut-3-en-1-yl *O*-Isopropyl Thionocarbonate (16)**. A solution of (*E*)-4-phenylbut-3-en-1-ol (560 mg, 3.6 mmol) and (thiocarbonyl)diimidazole (900 mg, 5.0 mmol) in THF (12 mL) was boiled for 40 min. The solvent was evaporated in vacuo and replaced by 2-propanol (30 mL) and the mixture boiled for 24 h. After evaporation of the solvent flash chromatography (hexane/EtOAc, 50:1) yielded 16 (575 mg, 61%) as a pale yellow oil: IR (film) 3027, 2983, 1495, 1450, 1376 and 1357, 1277–1237 vs, br, 1176, 1110, 1064, 967, 913, 745, 694 cm^{-1}; ^1H NMR (80 MHz) δ 1.36 (d, J = 6.2 Hz, 6 H, Me_2CH), 2.66 (apparent q, J = 6.4 Hz, 2 H, $CHCH_2CH_2O$), 4.53 (t, J = 6.8 Hz, 2 H, CH_2CH_2O), 5.43 (quint, J = 6.2 Hz, 1 H, Me_2CH), 5.8–6.6 (m, 2 H, PhCH=$CHCH_2$), 7.29 (Ph); UV λ (CH_2Cl_2) 247 (19 900), 284 (1485), 293 nm (995). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.18; H, 7.25; S, 12.79. Found: C, 67.48; H, 7.01; S, 13.29.

***O*-(*E*)-4-Phenylbut-3-enyl *O*-Phenyl Thionocarbonate (17)**. Phenyl chlorothionoformate (0.56 mL, 3.1 mmol) was added to a solution of 4-phenylbut-3-en-1-ol (413 mg, 2.8 mmol) and pyridine (0.8 mL) in CH_2Cl_2 (18 mL). After 15 min the reaction was worked up as usual and flash chromatography (hexane/EtOAc, 50:1) yielded 17 (728 mg, 92%): IR (film) 3029, 2956, 1592, 1491, 1387, 1284–1275br, s, 1211–1197br, s, 1005, 967, 772, 746, 690 cm^{-1}; ^1H NMR δ 2.74 (apparent q, J = 6.7 Hz, 2 H, $CHCH_2CH_2O$), 4.64 (t, J = 6.7 Hz, 2 H, CH_2CH_2O), 6.22 (dd, J = 15.8, 7.0 Hz, 1 H, PhCH=CH), 6.53 (d, J = 15.8 Hz, 1 H, PhCH), 7.08–7.49 (m, 10 H); UV λ_{max} (CH_2Cl_2) 247 (20 000), 284 (1495), 293 nm (990). Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67; S, 11.27. Found: C, 71.62; H, 5.38; S, 11.46.

***(Z)*-4-Phenylbut-3-enyl Thionobenzoate (18)**. Treatment of (*Z*)-4-phenylbut-3-en-1-ol (0.83 g, 5.6 mmol) with ((thiobenzoyl)thio)acetic acid (1.20 g, 5.6 mmol) according to the procedure of Barton[1] gave after flash chromatography (CH_2Cl_2/hexane, 1:3) the title compound 18 (1.12 g, 75%) as a yellow oil: IR (CH_2Cl_2) 1596 (Ar), 1235, 1273 cm^{-1}; ^1H NMR (80 MHz) δ 2.93 (apparent dq, J = 6.9, 1.4 Hz, 2 H, CH=$CHCH_2CH_2$), 4.74 (t, J = 6.7 Hz, 2 H, CH_2CH_2O), 5.70 (dt, J = 11.5, 6.8 Hz, 1 H, CH_2CH=CH), 6.62 (d, J = 11.6 Hz, CH=CHPh), 7.32–7.53 (m, 8 H, ArH), 8.14 (dd, J = 7.6, 1.7 Hz, 2 H, ArH). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01; S, 11.95. Found: C, 75.97; H, 6.00; S, 12.07.

(21) Barton, D. H. R.; Motherwell, W. B.; Stange, A. *Synthesis* **1981**, 743.

***O*-4-Phenylbut-3-yn-1-yl *S*-Methyl Dithiocarbonate (19).** Carbon disulfide (33 mL) was added to a stirred solution of 4-phenylbut-3-yn-1-ol (1.02 g, 7 mmol) and DBN (3.8 g) in DMF (33 mL). A deep red color appeared immediately, and after 1 h methyl iodide (66 mL) was added. Stirring was continued for a further 1 h, and then carbon disulfide and methyl iodide were removed under reduced pressure. The residue was dissolved in a mixture of EtOAc and toluene (600 mL, 2:1) and washed with water (7 × 150 mL) and brine (100 mL). The organic layer was dried, and the solvent was removed. Flash chromatography of the residue (hexane/EtOAc, 30:1), followed by distillation (90 °C (0.2 mmHg)) yielded the dithiocarbonate **19** (1.22 g, 78%) as a pale orange oil; IR and ^{1}H NMR data are in complete agreement with the literature.[19]

3(*E*)-Benzylidene-4,5-dihydrofuran-2(3*H*)-thione (58). A solution 3(*E*)-benzylidene-4,5-dihydrofuran-2(3*H*)-one (78 mg, 0.45 mmol) and the Lawesson reagent[22] (212 mg, 0.48 mmol) were refluxed in xylene (4 mL) for 3 h. The solvent was evaporated and flash chromatography of the residue (hexane/CH_2Cl_2, 3:1) yielded the title compound **58** (76 mg, 88%) as yellow crystals. IR and ^{1}H NMR data are in complete agreement with literature.[19]

[[((*E*)-4-Phenylbut-3-en-1-yl)oxy](thiocarbonyl)]pyyrolidine (20). A solution of *S*-methyl dithiocarbonate **12** (369 mg, 1.55 mmol) in pyrrolidine (10 mL) was stirred at room temperature for 30 min. The excess pyrrolidine was evaporated in vacuo, and flash chromatography of the residue (hexane/EtOAc, 15:1) yielded **20** (360 mg, 89%) as a pale yellow oil: IR (film) 2976, 2877, 1477–1454vs, br, 1335, 1261s, 1224s, 1181, 1152, 1050, 967, 746, 695 cm^{-1}; ^{1}H NMR δ 1.91–1.98 (m, 4 H, $(CH_2)_2CH_2N$), 2.60–2.67 (m, 2 H, CH_2CH_2O), 3.51 (br t, J = 6 Hz, 2 H), 3.72 (br, t, J = 6 Hz, 2 H), 4.57 (t, J = 6.55 Hz, 2 H, CH_2O), 6.21 (dt, J = 15.8 and 6.9 Hz, 1 H, PhCH=C**H**), 6.48 (d, J = 15.8 Hz, 1 H, PhC**H**), 7.19–7.41 (m, 5 H); UV λ_{max} (CH_2Cl_2) 250 (28000), 285 (infl) (3000), and 294 nm (infl) (1260); MS m/e 130 (100), 129 (40), 115 (23), 55 (26). Anal. Calcd for $C_{15}H_{19}NOS$: C, 68.94; H, 7.33; N, 5.36. Found: C, 67.02; H, 7.71; N, 5.71.

1-(4-Morpholino(thiocarbonyl))-2-[((*E*)-4-Phenylbut-3-en-1-yl)oxy]benzene (22). A solution of 1-(4-morpholinocarbonyl), 2-[((*E*)-4-phenylbut-3-en-1-yl)oxy]benzene (6.60 g, 20 mmol), and (*p*-methoxyphenyl)thionophosphine sulfide (Lawesson's Reagent) (4.04 g, 10 mmol) in dry toluene was warmed to 90 °C[22] until consumption of staring material (monitored by TLC). Flash chromatography of the residue obtained after removal of the solvent afforded the title compound **22** (5.00 g, 75%) as a pale yellow solid: recrystallized from ethanol, mp 114–115 °C, ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.38–3.72 (m, 4 H, CH_2NCH_2), 3.78–3.90 (m, 2 H, CHHO), 4.40–4.52 (m, 2 H, CHHO), 4.73 (d, J = 5 Hz, 2 H, OCH_2CH=CHPh), 6.33 (dt, J = 16, 5.1 Hz, 1 H, OCH_2CH=CHPh), 6.74 (d, J = 16 Hz, 1 H, OCH_2CH=C**H**Ph), 6.87–7.42 (m, 9 H, Ar**H**); IR (CH_2Cl_2) 1597, 1481, 1231 cm^{-1}; HRMS m/e calcd for $C_{20}H_{21}NO_2S$ 339.1286, found 339.1299; MS m/e 339 (M^+), 306 ($M - SH^+$), 117 ($CH_2CHCHPh^+$), 91 (CH_2Ph^+), 86 (morpholine$^+$). Anal. Calcd for $C_{20}H_{21}NO_2S$: C, 70.76; H, 6.23; N, 4.13; S. 9.44. Found: C, 70.76; H, 6.24; N, 4.11; S, 9.31.

1-[(*E*)-4-Phenylbut-3-en-1-yl]-5-thioxopyrrolidin-2-one (23) was prepared as described for thioamide **22** from 1-((*E*)-4-phenylbut-3-en-1-yl)-2,5-pyrrolidinedione and Lawesson's reagent (100 °C, 1 h) in 89% yield; mp 78–79 °C (from methylene chloride/hexane): IR (CH_2Cl_2) 1752, 1342 cm^{-1}; ^{1}H NMR δ 2.52–2.61 (m, 2 H, CH_2CH_2CH=CH), 2.64–2.70 (m, 2 H, 3-CH_2), 3.07–3.13 (m, 2 H, 4-CH_2), 4.04 (t, J = 6, 16 Hz, 1 H, CH_2CH=CHPh), 6.39 (d, J = 15.8 Hz, 1 H, CH=C**H**Ph), 7.22–7.23 (m, Ph); HRMS calcd for $C_{14}H_{15}NOS$ 245.0869, found m/e 245.0873 (M^+), 130 (PhCH=CHCH=CH), 115 (C_4H_5NOS).

***N*-[(*E*)-4-Phenylbut-3-en-1-yl]thiosaccharin (24)** was prepared as described for thioamide **22** from 1-((*E*)-4-phenylbut-3-en-1-yl)sacchain and Lawesson's reagent (110 °C, 1 h): 96% yield; mp 117–119 °C (from ethyl acetate/hexane); IR (CH_2Cl_2) 1341, 1184 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.86 (dq, J = 1.2, 7 Hz, CH_2CH_2CH=CH), 4.24 (m, 2 H, NCH_2CH_2), 6.23 (dt, J = 7, 16 Hz, 1 H, CH_2CH=CHPh), 6.52 (d, J = 16 Hz, 1 H, CH_2CH=C**H**Ph), 7.18–7.37 (m, Ph), 7.74–7.84 and 8.20–8.26 (4 H, Ar); HRMS calcd for $C_{17}H_{15}NO_2S$ 329.0538, found m/e 329.0543 (M^+), 130 (PhCH=CHCH=CH), 117 (PhCh=$CHCH_2$).

General Procedures for the Reaction of Unsaturated Thiocarbonyl Compounds with *n*-Bu_3SnH. Seven similar procedures were used for the reactions described in Table I. **(A)** Individual solutions of *n*-Bu_3SnH (1.15 equiv) and AIBN (0.15 equiv) in 10 mL of benzene were added over 1.5–2 h to a boiling 0.02 M solution of the thiocarbonyl compound in benzene. The mixture was then refluxed until TLC indicated complete consumption of the thiocarbonyl compound. The solvent was evaporated and the residue was purified by flash chromatography. **(B)** A solution of the thiocarbonyl compound (1 equiv, 0.02 M), *n*-Bu_3SnH (1.15 equiv), and AIBN (0.15 equiv) in benzene was boiled until TLC indicated complete consumption of starting material. Purification as in A. **(C)** As in A but in boiling toluene. **(D)** As in A but using 2.3 equiv of *n*-Bu_3 SnH. **(E)** As in B but in boiling toluene. **(F)** As in B but in boiling xylene. **(G)** As in A but in boiling xylene.

3-Benzyl-4,5-dihydrofuran-2(3*H*)-thione (25). Cyclization of dithiocarbonate **12** according to procedure A (and additional heating for 30 min) or B afforded **25** as pale yellow prisms: mp 70 °C; IR (CH_2Cl_2) 3031, 2913, 1604, 1497, 1455, 1242, 1191 cm^{-1}; ^{1}H NMR δ 1.88–2.03 (m, 1 H, 4-CH), 2.20–2.32 (m, 1 H, 4′-CH), 2.71 (dd, J = 13.8, 10.0 Hz, 1 H, PhCHH′), 3.07–3.19 (m, 1 H, 3-CH), 3.54 (dd, J = 13.9, 4.2 Hz, 1 H, PhCH′**H**), 4.39–4.56 (m, 2 H, CH_2O), 6.98–7.58 (m, 5 H, ArH); UV λ_{max} (CH_2Cl_2) 251 (13700), 309 nm (2600); MS m/e 192 (27, M^+), 131 (73), 103 (24), 91 (100), 65 (42), 51 (28); HRMS calcd for $C_{11}H_{12}OS$ m/e 192.0609, found m/e 192.0618. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.67. Found: C, 68.81; H, 6.17; S, 16.27.

3-Methyl-4,5-dihydrofuran-2(3*H*)-thione (26). Cyclization of dithiocarbonate **13** according to procedure B afforded **26**: NMR δ 1.42 (d, J = 7.0 Hz, 3 H, CH_3), 1.84–2.00 (m, 1 H), 2.45–2.56 (m, 1 H), 2.86–2.96 (m, 1 H), 4.50 (td, J = 9.6, 6.6 Hz, 1 H), 4.65 (td, J = 9, 3.2 Hz, 1 H); MS m/e (relative intensity) 116 (M^+, 85), 71 (12), 56 (47), 55 (100); HRMS calcd for C_5H_8OS m/e 116.0296, found m/e 116.0305.

Reaction of Dithiocarbonate 14 with *n*-Bu_3SnH. In this reaction (procedure B) the starting material is consumed, but only traces of 3,3′-dimethyl thionobutyrolactone (**27**) were produced [NMR δ 1.34 (s, 6 H), 2.17 (t, J = 7.1 Hz, 2 H), 4.56 (t, J = 7.1 Hz, 2 H); MS, m/e 130 (M^+, 29), 115 (9), 69 (16), 55 (100)].

3-(Diphenylmethyl)-4,5-dihydrofuran-2(3*H*)-thione (28). Cyclization of thiocarbonate **17** according to procedures A and E, and additional heating for 30 min, afforded products **28**, **29**, and **25** (see Table I, entries 7 and 8). Data for **28**: IR (film) 3028, 2912, 1766vs, 1601, 1153, 1027 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.01–2.11 (m, 1 H, CHH′CH_2O), 2.29–2.41 (m, 1 H, CH′**H**CH_2O), 3.43 (dt, J = 9.1, 6.8 Hz, 1 H, CHC=O), 3.97 (dt, J = 8.7, 4.0 Hz, 1 H, CHH′O), 4.13 (dt, J = 8.7, 7.2 Hz, 1 H, CH′HO), 4.46 (d, J = 6.8 Hz, 1 H, Ph_2CH), 7.16–7.44 (m, 10 H); mass spectrum, m/e 252 (M^+, 4), 167 (PhCHPh, 100), 165 (31), 115 (23), 91 (25), 77 (28); HRMS calcd for $C_{17}H_{16}O_2$ m/e 252.1150, found m/e 252.1158. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.97; H, 6.29.

4,5-Dihydro-2-phenyl-3-benzylfuran (30). Cyclization of thionobenzoate **18** according to procedure C (and additional heating for 20 h) gave the title compound **30**: IR (film) 1710 (ArC=C) cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.60 (t, J = 8.5 Hz, 2 H, OCH_2CH_2), 3.60 (s, 2 H, CH_2Ph), 4.29 (t, J = 8.5 Hz, 2 H, OCH_2), 7.09–7.41 (m, 10 H, Ar**H**); HRMS calcd for $C_{17}H_{16}O$ 236.1197, found m/e 236.1210. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.32; H, 6.82.

Cyclization of 1-(4-Morpholino(thiocarbonyl))-2-[((*E*)-4-phenylbut-3-en-1-yl)oxy]benzene (22). The reaction was performed according to procedure G with an additional heating for 5 h. Flash chromatography (methylene chloride–hexane, 1/1) afforded the following: (a) 3-Benzyl-4-chromanone (**31**) (10%); mp 64–65 °C (ethyl acetate–hexane) (lit.[23] mp 56 °C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.69–3.09 (m, 2 H, CHC=O + CHHPh), 3.3 (dd, J = 12.2, 3.5 Hz, 1 H, CHHPh), 4.03–4.33 (m, 2 H, OCH_2), 6.82–7.72 (m, 8 H, Ar**H**), 7.92 (dd, J = 7.8, 1.5 Hz, 1 H, Ar**H** α to C=O); IR (CH_2Cl_2) 1689, 1606 cm^{-1}; HRMS m/e calcd for $C_{16}H_{14}O_2$ 238.0990, found 238.0980; MS m/e 238 (M^+), 147 (M

(22) Scheibye, S.; Pedersen, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229.

(23) Pfeiffer, P.; Grimm, K.; Schmidt, H. *Liebigs Ann. Chem.* **1949**, *564*, 208.

– CH_2Ph^+), 133 (M – $C_6H_5CO^+$), 120 ($OC_6H_4CO^+$), 105 ($C_6H_5CO^+$), 91 (CH_2Ph^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.67; H, 5.88. (b) 4-Chromanone (**32**) (32%).

Cyclization of 1-[(*E*)-4-Phenylbut-3-en-1-yl]-5-thioxopyrrolidin-2-one (23). The reaction was performed according to procedure F and stopped after 40 min. Flash chromatography (ethyl acetate–hexane, 3/1) of the crude obtained after evaporation of the solvent afforded starting material (**23**) (14%) and 1-aza-4-benzylbicyclo[3.3.0]oct-4-en-8-one (**33**) (54%): IR (CH_2Cl_2) 1681 cm^{-1}; ^1H NMR δ 2.34–2.44 and 2.7 (2 m, 4 H, 6-CH_2 and 7-CH_2), 2.8 (m, 2 H, 3-CH_2), 3.33 (s, 2 H, $PhCH_2$), 3.61 (t, J = 8.7 Hz, 2 H, 2-CH_2), 7.15–7.33 (m, Ph); ^{13}C NMR (270 MHz) δ 17.81, 33.50, 34.68, 39.88, 110.34, 126.33, 128.51, 128.64, 139.18, 140.3, and 170.33; HRMS m/e M^+ 213.1169 (calcd for $C_{14}H_{15}NO$ 213.1149.1286), 136 (M^+ – Ph), 122 (M^+ – $PhCH_2$).

Cyclization of 1-((*E*)-4-Phenylbut-3-en-1-yl)thiosaccharin (24). The reaction was performed according to procedure E for 30 min, flash chromatography (ethyl acetate–hexane, 1/6) of the crude obtained after evaporation of the solvent afforded the tributyltin derivative **34** (54%): mp 118–120 °C (methylene chloride/hexane); IR (CH_2Cl_2) 1171, 1247 cm^{-1}; ^1H NMR δ 0.81–1.41 (m, 27 H, *n*-Bu_3Sn), 2.1–2.3 (m, 2 H), 2.3–2.45 (m, 1 H), 2.92–3.15 (m, 2 H), 3.31–3.39 (m, 1 H), 3.71–3.81 (m, 1 H), 7.05–7.25 (m, Ph), 7.75–7.73 (m, 4 H, Ar). Anal. Calcd for $C_{29}H_{43}NO_2S_2Sn$: C, 56.1; H, 7.0; N, 2.3; S, 10.3. Found: C, 55.8; H, 6.6; N, 2.4; S, 10.1.

Pyrrolinodihydrobenzisothiazole, 35. Conversion of **34** into **35** with TFA is quantitative, and the reaction can be performed using the crude reaction mixture from the cyclization of **24**. Thus, when cyclization of **24** (1 mmol) was completed (TLC), the reaction mixture was cooled to room temperature and stirred with TFA (2 mL) for 4 h. The reaction mixture was then neutralized with a saturated $NaHCO_3$ solution. Flash chromatography (ethyl acetate–hexane, 1/6) of the crude obtained after standard workup afforded the pyrrolinodihydrobenzisothiazole (**35**) (60%): mp 140 °C; IR (CH_2Cl_2) 1161, 1263 cm^{-1}; ^1H NMR δ 2.93 (t, J = 8.5 Hz, 2 H), 3.69 (t, J = 8.4 Hz, 2 H), 3.84 (s, 2 H, $PhCH_2$), 7.20–7.51 (m, Ph), 7.53–7.85 (m, 4 H, Ar). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.7; H, 5.1; N, 4.7; S, 10.8. Found: C, 68.6; H, 5.0; N, 4.7; S, 10.7.

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Preparation of (*p*-Phenylene)bis(aryliodonium) Ditriflates and Their Double Substitution by Some Nucleophiles

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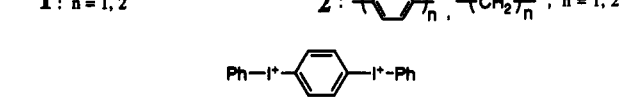
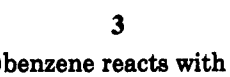
A reagent prepared from a 1:1 molar mixture of PhIO and Tf_2O or from a 1:2 molar mixture of PhIO and TfOH shows high reactivity toward aromatic substrates and gives (*p*-phenylene)bis(aryliodonium) ditriflates (**8**). Interaction of the reagent [PhIO–Tf_2O] with cyclohexene suggests that it has a *p*-[phenyl[(trifluoromethanesulfonyl)-oxy]iodo]phenyliodine(III) structure. Reactions of (*p*-phenylene)bis(aryliodonium) ditriflates with pyridine, triphenylphosphine, or diphenyl sulfide give doubly para-substituted benzene derivatives in good to high yields.

Much attention has recently been paid to the utilization of iodine(III) compounds for organic synthesis.[1] Iodine(III) compounds containing aryl, alkenyl, alkynyl, and fluoroalkyl ligands are most conveniently prepared from reagents bearing the phenyliodonio [PhI(III)] group. The phenyliodonio group is highly sensitive to replacement by nucleophiles and useful for the introduction of functional groups. If polyphenyliodinated compounds are employed, one can introduce polyfunctionality into the substrate. Recently, Stang and co-workers[2] have prepared bis-iodonium compounds of types **1** and **2** which can be used for the introduction of bifunctionality. *p*-Phenylene bis-iodonium salts **3** are also known,[3] having been prepared by the oxidation of 1,4-diiodobenzene to 1,4-bis(diacetoxyiodo)benzene and subsequent condensation of the latter with benzene in the presence of concentrated H_2SO_4. However, little attention has been paid to the synthesis and reactions of these compounds.



1: n = 1, 2

2: n = 1, 2



3

(Diacetoxyiodo)benzene reacts with triflic acid to give μ-oxybis[(trifluoromethanesulfonyl)oxy](phenyl)iodine] (**4**)[4] known as Zefirov's reagent. Zefirov's reagent can also

(1) For recent reviews: Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377. Umemoto, T. *Yuki Gosei Kagaku Kyokai Shi* **1983**, *41*, 251. Koser, G. F. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons, New York, 1983; Chapters 18 and 25. Varvoglis, A. *Synthesis* **1984**, 709. Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. Ochiai, M.; Nagao, Y. *Yuki Gosei Kyokai Shi* **1986**, *44*, 660. Merkushev, E. B. *Russ. Chem. Rev.* (*Eng. Transl.*) **1987**, *56*, 826. Ochiai, M. *Rev. Heteroatom Chem.* **1989**, *2*, 92. Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274. Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers, Inc.: New York, 1992.

(2) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1990**, *112*, 6437. Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4571. Stang, P. J.; Tykwinski, R.; Zhdankin, V. V. *J. Org. Chem.* **1992**, *57*, 1861. Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411.

(3) Yamada, Y.; Kashima, K.; Okawara, M. *J. Polym. Sci. Polym. Lett. Ed.* **1976**, *14*, 65.

(4) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Koz'min, A. S. *J. Org. Chem. USSR* (*Engl. Transl.*) **1984**, *20*, 401. Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Sorokin, V. D.; Semerikov, V. N.; Koz'min, A. S.; Caple, R.; Berglund, B. A. *Tetrahedron Lett.* **1986**, *27*, 3971.

0022-3263/92/1957-6810$03.00/0