REVIEW

Homolytic Substitution at the Sulfur Atom as a Tool for Organic Synthesis

by **David Crich**

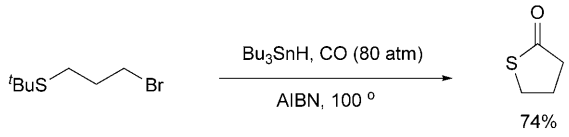
Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, IL 60607-7061, U.S.A.

Dedicated to the memory of Professor *Hanns Fischer*

The use of intramolecular homolytic substitution at the sulfur atom by aryl and vinyl radicals, as an alternative to the use of alkyl halides, and chalcogenides as radical precursors in organic synthesis is reviewed.

Introduction. – Traditionally, the precursors of choice for alkyl radicals in preparative radical chain reactions have been the alkyl halides, especially bromides and iodides [1–10]. However, the heterolytic leaving-group ability of the halides renders their use as radical precursors impractical in many instances. In such circumstances, as demonstrated by *Clive* and co-workers [11], the alkyl aryl chalcogenides have many advantages. As a rule of thumb, the alkyl phenyl selenides have comparable reactivity to the alkyl bromides, whereas the more reactive alkyl phenyl tellurides mimic the reactivity of alkyl iodides as precursors for alkyl radicals under typical stannane-mediated reaction conditions [12–14]. Completing the trend, the alkyl phenyl sulfides, with their stronger C–S bonds, have comparable reactivity to the alkyl chlorides [12], thus, it is not surprising that they have seen comparatively little use in preparative radical chemistry. Perceived toxicity issues with organoselenium and organotellurium compounds, however, provide a strong incentive to develop methods to increase the reactivity of the more palatable organosulfur compounds. In our laboratory, this led to the exploration and development of intramolecular homolytic substitution processes at the sulfur atom, as set out in this review. The work described herein, with the focus on applications of the expelled radical, is distinct from numerous studies of intramolecular homolytic substitution at the sulfur atom conducted with a view to the synthesis of S-based heterocycles [15–19], illustrated by the carbonylative cyclizations of *Ryu* and co-workers (*Scheme 1*; AIBN = 2,2′-azobis[2-methylpropanenitrile]) [20].

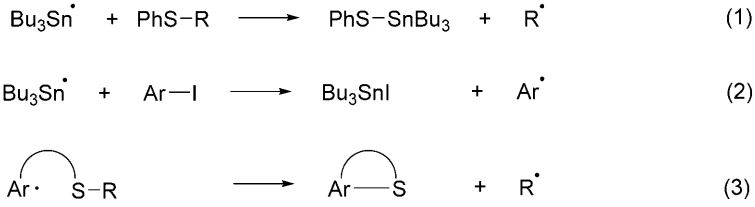
Scheme 1



AIBN = $NCC(Me)_2N{=}NC(Me)_2CN$

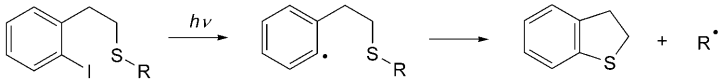
Discussion. – It is an under-appreciated fact that one slow propagation step in a radical chain sequence may often be advantageously replaced by two rapid, efficient steps. Excellent examples of this philosophy are to be found in the concept of polarity-reversal catalysis advanced by *Roberts* [21], and in the catalysis of certain stannane-mediated radical chain reactions by selenols [22–24].

In extending this concept to radical generation from alkyl and acyl sulfides, we sought to replace the slow reaction of stannyl radicals with the sulfides themselves (*Eqn. 1*) by the combination of the rapid reaction of an aryl iodide with stannyl radicals (*Eqn. 2*) [13], and a subsequent intramolecular homolytic substitution at the S-atom with expulsion of the desired alkyl radical (*Eqn. 3*).

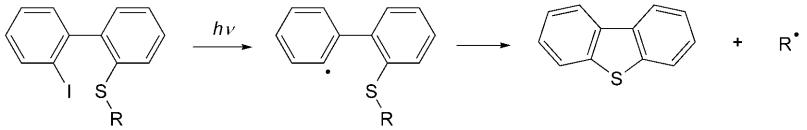


In this endeavor, we drew on the prior art in the form of extensive physical organic studies of homolytic substitution processes at the S-atom, as reviewed in 1971 by *Ingold* and *Roberts* [18], and in 1995 by *Schiesser* and *Wild* [15]. Importantly, it had been demonstrated by *Kampmeier* and co-workers that the cyclization of aryl radicals onto sulfides takes place with cleavage of the exocyclic bond in systems with both alkyl and aryl tethers (*Schemes 2* and *3*) [25][26]. *Tundo* and co-workers subsequently confirmed this result for the biphenyl system, but using an arenediazonium salt as radical precursor (*Scheme 4*) [27]. Rate constants for the cyclization of alkyl and aryl radicals on sulfides with the expulsion of the exocyclic group were determined by the groups of *Beckwith* and of *Franz* as reported in *Table 1* [28–30].

Scheme 2



Scheme 3



Scheme 4

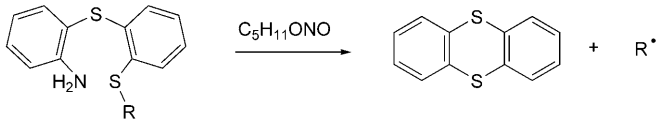
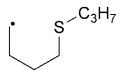
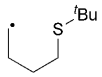
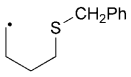
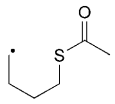
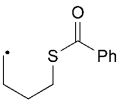
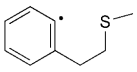
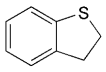
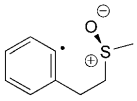
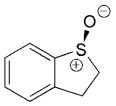
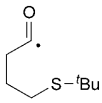
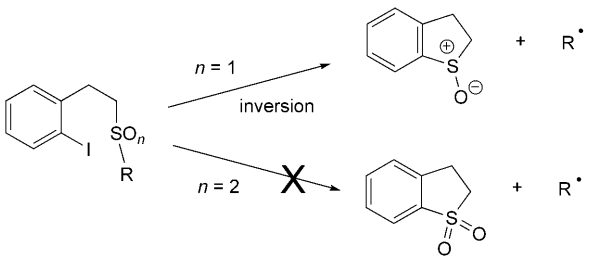


Table 1. *Representative Kinetic Data*

Substrate	T (°)	Product	k [s^{-1}]	Ref.
	25		18.2	[29]
	25		$2.74 \cdot 10^2$	[29]
	25		$3.91 \cdot 10^3$	[29]
	50 104		$2.0 \cdot 10^2$ $2.3 \cdot 10^2$	[28]
	50 104		$7.0 \cdot 10^2$ $1.1 \cdot 10^3$	[28]
	80		$5 \cdot 10^7$	[30]
	80		$> 3 \cdot 10^8$	[30]
	25		$7.5 \cdot 10^3$	[20]

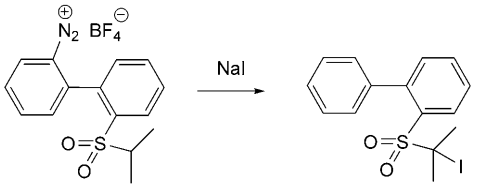
Following an early report on the cyclization of an aryl radical onto a sulfoxide, again with expulsion of the exocyclic group [26], *Beckwith* and *Boate* conducted a more detailed investigation and established that the sulfoxide reaction proceeds with inversion of configuration and is considerably more rapid than attack on the analogous sulfide (*Scheme 5*, *Table 1*) [30]. Cyclization at the sulfoxide S-atom, with expulsion of the exocyclic radical, was also demonstrated by *Maruoka* and co-workers in a 2-(alkylthio)-2′-iodo-1,1′-biphenyl system [31]. Notably, however, *Kampmeier* and co-workers reported that the reaction cannot be extended to sulfones (*Scheme 5*) [26].

Scheme 5



Notwithstanding reports to the contrary from *Fuchs'* laboratory [32][33], it has again been demonstrated recently that intramolecular homolytic substitution at the sulfonyl S-atom is not a viable process [34]. For example, the major product from the reaction of the diazonium salt **1** with iodide ion was the α-sulfonyl iodide **2** (*Scheme 6*). This product results from H-atom abstraction by the aryl radical through a seven-membered cyclic transition state, followed by trapping with iodine. No evidence was found for the formation of dibenzothiophene *S*,*S*-dioxide, the anticipated product of homolytic substitution at the S-atom. When H-atom abstraction was suppressed by use of a *tert*-butyl sulfone, the aryl radical underwent cyclization onto the sulfonyl O-atom in preference to attack at the sulfonyl S-atom [34].

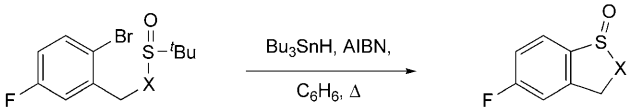
Scheme 6



1 **2** (49%)

However, in the line with the successful cyclizations at the sulfoxide S-atom, it has been shown that aryl-radical cyclization on sulfur(IV) in sulfinate esters and sulfinamides is a useful means of preparation of S-based heterocycles (*Scheme 7*) [35].

Scheme 7



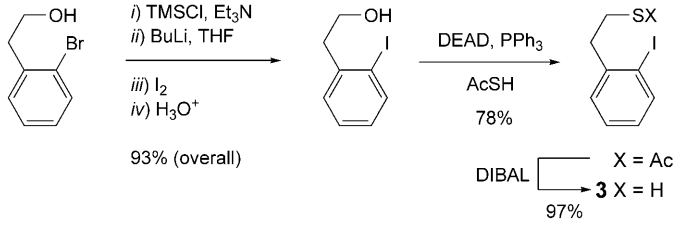
X = O, 95%
X = NH, 85%

AIBN = $NCC(Me)_2N{=}NC(Me)_2CN$

On the basis of the above, we selected a system employing an alkyl tether between the aryl iodide and the sulfide and, because of our interest in acyl radicals [36], focused our attention on the use of thiol-derived esters. Two thiols, **3** and **4**, were synthesized (*Schemes 8* and *9*), differing only by the presence of a *gem*-dimethyl group in the latter, which was included with a view to accelerate the rate of the ring-closure step and, therefore, to minimize the premature quenching of the aryl radical [37]. In subsequent work we have also successfully employed the aryl bromide corresponding to the *gem*-dimethyl-substituted system **4** as alkyl radical precursor [38][39].

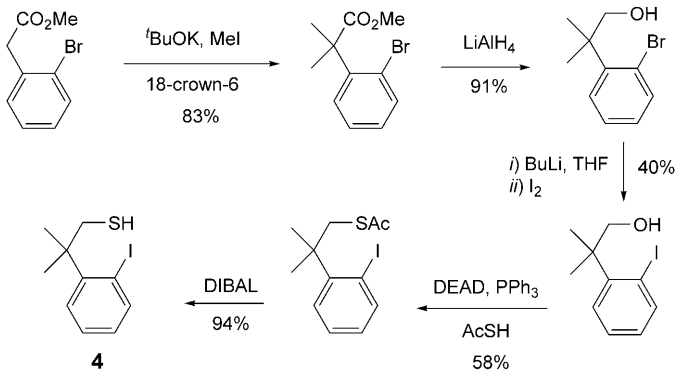
A series of thiol-derived esters were then synthesized either by reaction of the thiols with acyl chlorides or by carbodiimide-mediated direct coupling of the thiol and the carboxylic acid. This series of thiol-derived esters was then subjected to reaction with

Scheme 8



TMSCl = Me_3SiCl, DEAD = EtOOCN=NCOOEt, DIBAL = diisobutylaluminium hydride

Scheme 9



DEAD = EtOOCN=NCOOEt, DIBAL = diisobutylaluminium hydride

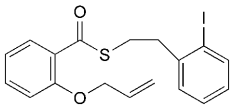
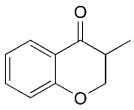
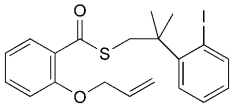
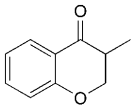
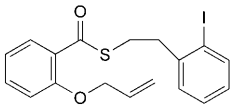
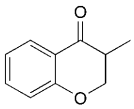
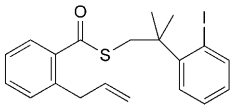
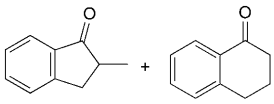
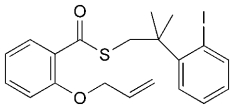
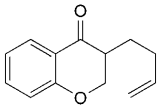
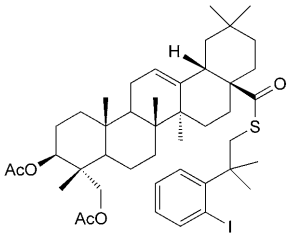
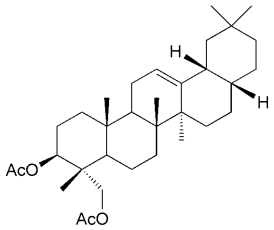
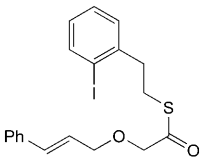
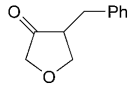
either tributylstannane, tris(trimethylsilyl)silane, or allyltributylstannane with AIBN initiation in benzene under reflux (*Table 2*) [37].

The influence of the *gem*-dimethyl group on the rate of the intramolecular homolytic substitution, and thus on the final yield of the acyl-radical cyclization, is apparent from a comparison of *Entries 1* and *2* in *Table 2*. The same effect may, however, be achieved by switching to the slower H-atom donor, tris(trimethylsilyl)silane as is clear from *Entry 3* (*Table 2*). On the whole, the yields of the various cyclizations and decarbonylation reactions depicted in *Table 2* are comparable to those obtained by stannane-mediated acyl-radical generation from acyl selenides [36].

(Iodoaryl)-thiol-derived esters have also served as acyl-radical precursors in carbohydrate chemistry. Thus, in a demonstration of the diastereoselective quenching of anomeric radicals, an ulosonic acid thiol-derived ester served as a precursor to the radical in question (*Scheme 10*) [40].

In a more elaborate demonstration of the power of radicals in synthesis, the synthesis of the rare and synthetically very challenging β-D-rhamnopyranosides, a modified benzylidene acetal **5** serves to control the diastereoselectivity of the glycosylation reaction, before undergoing radical fragmentation to give the rhamnopyranoside **6**, triggered by the initial homolytic substitution reaction [41][42]. The complex sequence of propagation steps involves, in addition to the homolytic substitution, decarbonylation, a kinetically preferred but contrathermodynamic cleavage of the primary C(6)–

Table 2. *Acyl Radical Generation and Cyclization under Reductive Conditions*

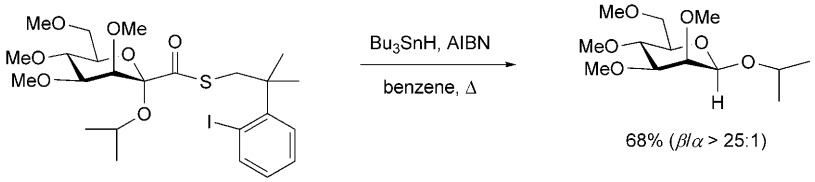
Entry	Substrate	Reagent	Product	Yield [%][a)][b)]
1		Bu_3SnH		96
2		Bu_3SnH		100
3		$(Me_3Si)_3SiH$		100
4				82 (96:4)
5		(allyl)Bu_3Sn		56
6		Bu_3SnH		92
7		Bu_3SnH		78

[a)] The mass balance is typically made up of the simple deiodinated substrate. [b)] Dihydrobenzothiophene or 3,3-dimethyldihydrobenzothiophene were formed as by-products in all reactions in yields corresponding to those of the cyclized products.

O(6) bond rather than of the secondary C(4)–O(4) bond, and chain transfer with the stannane (*Scheme 11*). The example of this class of transformation provided in *Scheme 12* is a particularly striking one as it involves the parallel fragmentation of two such systems in the course of a single reaction [42].

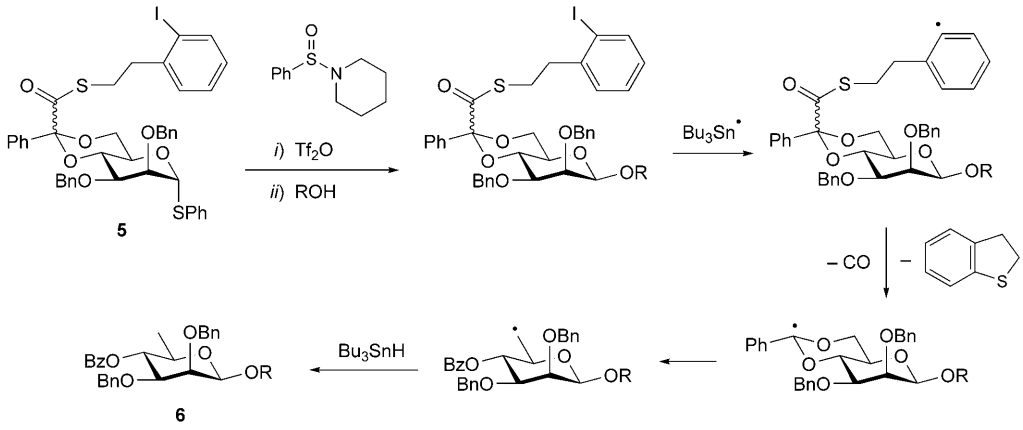
In some very elegant applications of radicals in polyquinane synthesis by the *Pattenden* group, iodoaryl-thiol-derived esters have served as precursors to α-ketenyl radicals, *i.e.*, geminally 2-oxoethenyl-substituted radicals (*Schemes 13* and *14*) [43][44].

Scheme 10



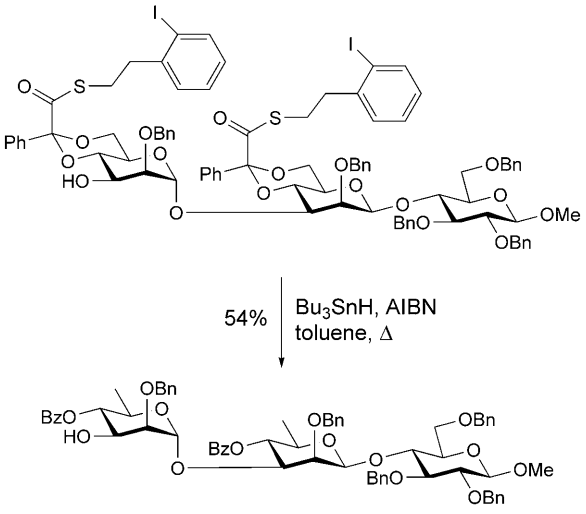
AIBN = $NCC(Me)_2N{=}NC(Me)_2CN$

Scheme 11



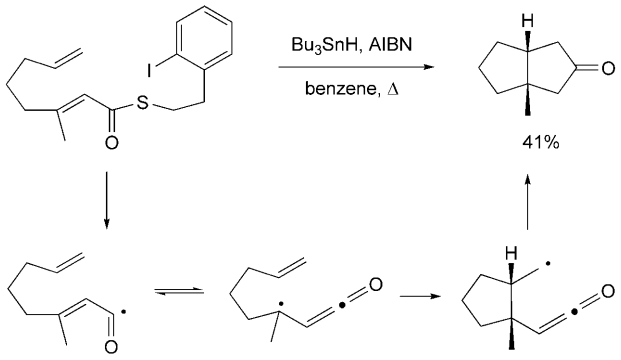
Tf = CF_3SO_2

Scheme 12



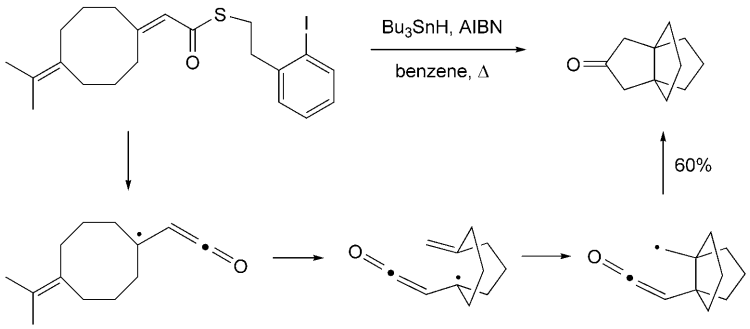
AIBN = $NCC(Me)_2N{=}NC(Me)_2CN$

Scheme 13



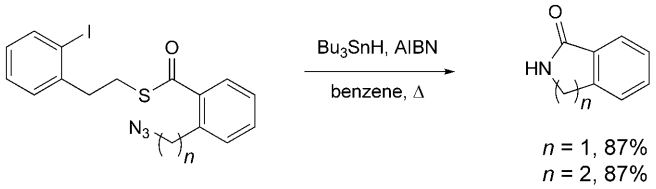
AIBN = $NCC(Me)_2N{=}NC(Me)_2CN$

Scheme 14



AIBN = $NCC(Me)_2N{=}NC(Me)_2CN$

Scheme 15

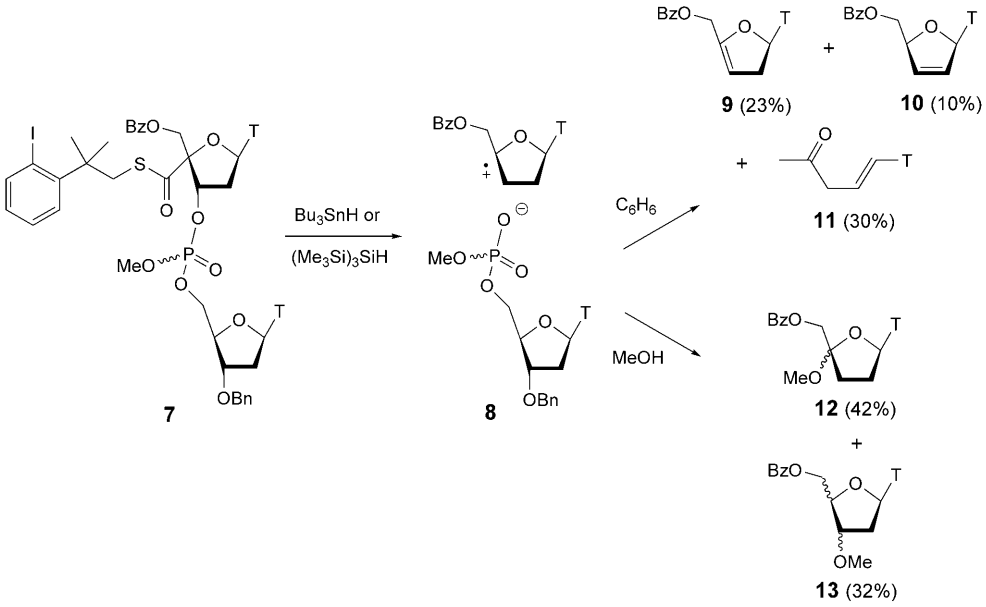


AIBN = $NCC(Me)_2N{=}NC(Me)_2CN$

The method was extended to the formation of lactams by *Spagnolo* and co-workers who induced the acyl radical to undergo cyclization onto a series of alkyl azides, as exemplified in *Scheme 15* [45]. When allyltributylstannane was used as the chain transfer agent, the corresponding *N*-allyl lactams were obtained albeit in modest yield.

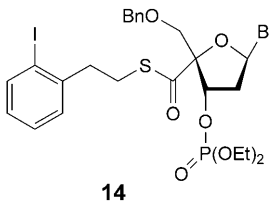
In a foray into nucleotide chemistry, the iodoaryl thioester trick was used to generate a nucleotide C(4′) radical from **7** [46]. This underwent fragmentation to the alkene radical cation/phosphate anion pair **8** [47–49], whose subsequent fate depended on the solvent. In benzene under reflux, deprotonation gave an allyl radical spanning the

Scheme 16



C(2′)–C(4′) positions, leading after chain transfer with tributylstannane to the two dihydrofurans **9** and **10**. Interestingly, the system also suffered a competing *retro*-5-*endo-trig* fragmentation to give the acyclic species **11** (*Scheme 16*). In MeOH solution, nucleophilic capture of the alkene radical cation followed by chain transfer giving products **12** and **13** was the major pathway (*Scheme 16*) [46].

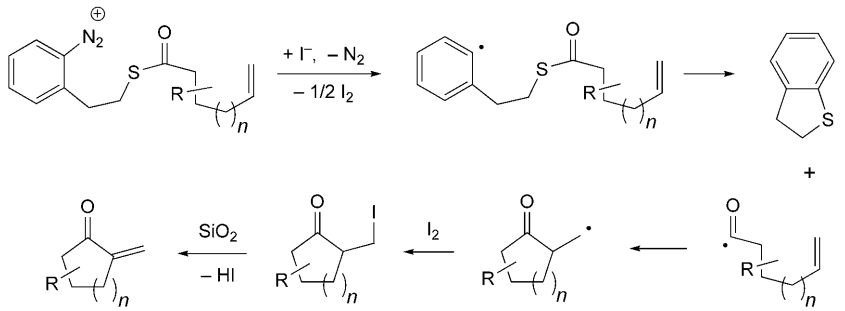
In an ensuing study designed to investigate the influence of the base on the rate of fragmentation of C(4′) radicals, thiol-derived esters **14** were used to trigger the fragmentation process [38]. In THF solution at 25°, fragmentation rates were found to vary between $2.6 \cdot 10^5\ s^{-1}$ for the adenosine derivative, and $7.3 \cdot 10^5\ s^{-1}$ for the cytidine derivative, with the thymidine derivative bracketed between these two. Fragmentation of the C(4′) radical derived from guanosine was too fast for determination of the rate constant by the competition kinetic methods employed, a fact that was attributed to perturbation of the dynamics of the radical cation/phosphate anion pair by electron transfer from the base [38].



14

A tin-free [50][51] method of generating acyl radicals from thiol-derived esters involves the formation of the sequence-initiating aryl radical by electron-transfer to an arenediazonium salt (*Scheme 17*) [52]. When the electron donor was iodide anion, the product of the radical sequence was an α-(iodomethyl)cycloalkanone, which suffered expulsion of iodide on passage over silica gel to give the α-methylenecycloalkanone.

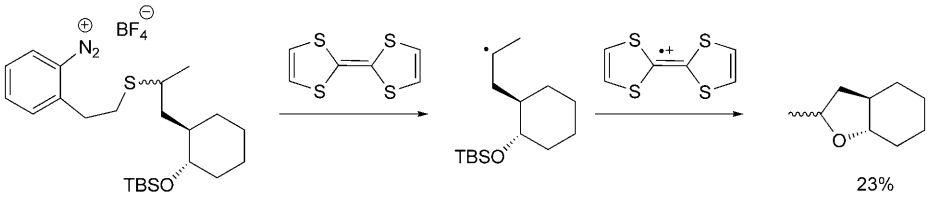
Scheme 17



A number of examples of this process were conducted (*Table 3*), including two in which the I-atom was retained in the product owing to the ultimate polar elimination being prevented (*Table 3*, *Entries 2* and *3*). Interesting aspects of this study include the change in regioselectivity between *Entries 4* and *5*, presumably due to reversibility of the initial '*exo*'-cyclization induced by extra stabilization of the acyl radical by the nitro group, and the use of alternative electron transfer/trapping reagents (*Entries 8* and *9*) [52].

In a demonstration of a radical/polar crossover experiment *Bashir* and *Murphy* employed an arenediazonium-ion-initiated homolytic substitution at the S-atom to generate an alkyl radical, which was then oxidized to the cation required for the ionic cyclization (*Scheme 18*) [53]. In this reaction sequence, tetrathiafulvalene serves as the electron donor to the diazonium salt, and the resulting radical cation as the oxidant for the alkyl radical [53].

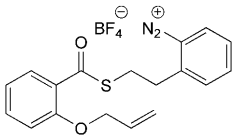
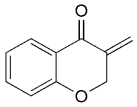
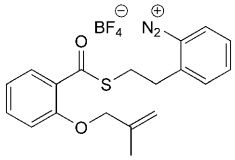
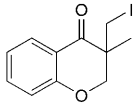
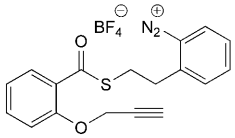
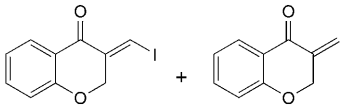
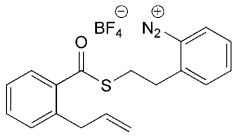
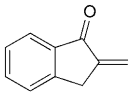
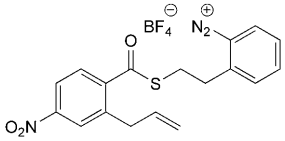
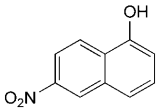
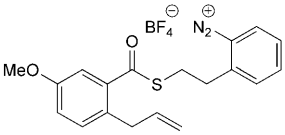
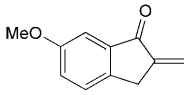
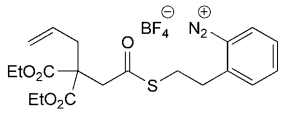
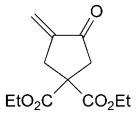
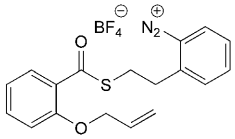
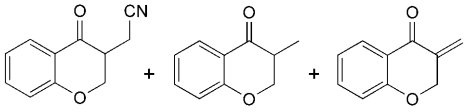
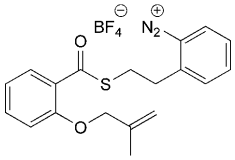
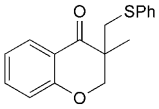
Scheme 18



TBS = ^{t}BuMe$_2$Si

Maruoka and co-workers have developed the 2-(alkylthio)-2′-iodo-1,1′-biphenyl system as a precursor to alkyl radicals [31]. The stability of the radical precursor in *Scheme 19* is noteworthy when compared to the putative corresponding alkyl iodide,

Table 3. *Acyl Radical Generation from Aryl Diazonium Salts*

Entry	Substrate	Reagent	Product(s)	Yield [%]
1		NaI		81
2		NaI		85
3		NaI		50 + 25
4		NaI		75
5		NaI		24
6		NaI		88
7		NaI		70
8		CuCN		36 + 12 + 12
9		NaSPh		35

and serves to illustrate one of the advantages of this method. Simple 2-(2-haloaryl)ethyl sulfides have also been used as precursors of alkyl radicals [39], and further examples of alkyl-radical generation in this general fashion are given in *Table 4* [31].

Scheme 19

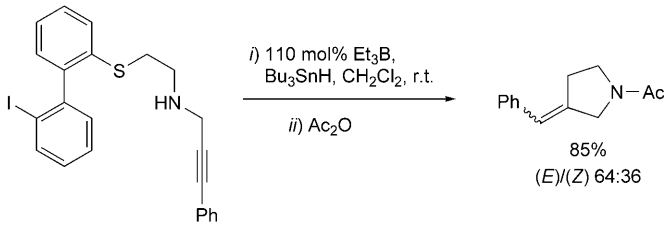
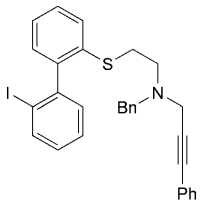
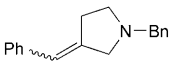
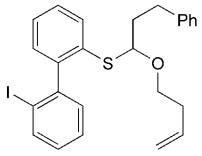
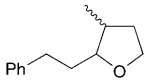
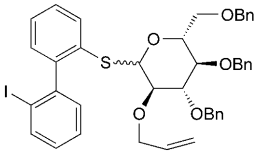
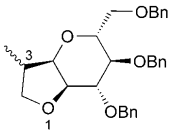
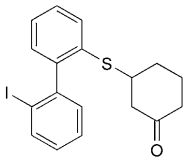
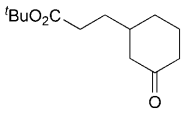
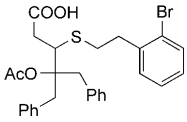
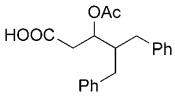


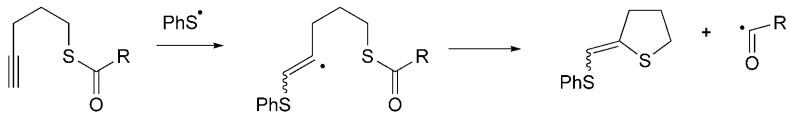
Table 4. *Radical Generation from Biaryl Iodides*

Substrate	Conditions	Product	Yield [%]
	Et_3B, Bu_3SnH, CH_2Cl_2, r.t.		87 (*E*)/(*Z*) 56:44
	Et_3B, Bu_3SnH, CH_2Cl_2, r.t.		84 *cis*/*trans* 94:6
	Et_3B, Bu_3SnH, CH_2Cl_2, r.t.		91 3α/3β 1:1
	Et_3B, Bu_3SnH, *tert*-butyl acrylate, CH_2Cl_2, r.t.		82
	Bu_3SnH, AIBN, C_6H_6, 80°		40

Spagnolo and co-workers have devised a very clever tin-free [50][51] variation of the general method, which does not rely on the use of an aryl iodide as the radical precursor but which makes use of a simple *S*-(pent-4-ynyl) ester [54][55]. Phenylthio rad-

icals add to the alkyne giving a vinyl radical which then triggers the homolytic substitution at the S-atom. Final chain transfer involves H-atom abstraction from thiophenol (*Scheme 20*). The method was applied to a wide variety of substrates with final chain transfer, after an acyl-radical cyclization, or directly to give aldehydes depending on the substitution pattern (*Table 5*) [54][55]. There would seem to be no reason why this method can not be applied to the preparation of alkyl radicals from alkyl *S*-(pent-4-ynyl) thioethers.

Scheme 20



Conclusions. – Intramolecular homolytic substitution at the S-atom is a viable alternative to the use of alkyl halides, and chalcogenides as a source of acyl and alkyl radicals for organic synthesis. A variety of sources of the attacking radical have been developed, providing the practitioner a choice of reaction conditions, and of chain-transfer steps.

Table 5. *Acyl Radical Generation by Thiyl Radical Addition to Alkynes*[a])

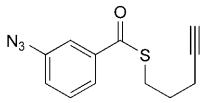
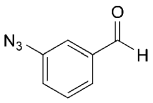
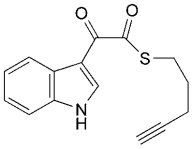
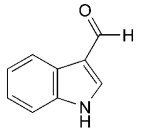
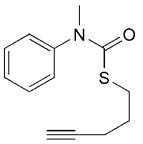
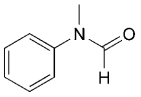
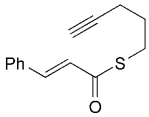
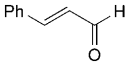
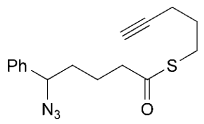
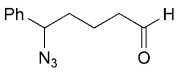
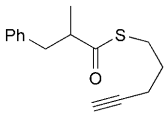
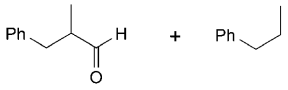
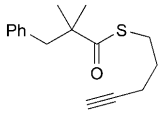
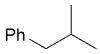
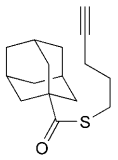
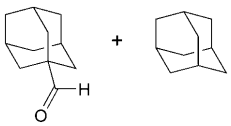
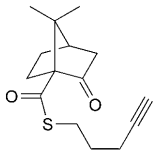
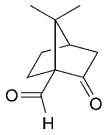
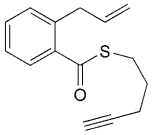
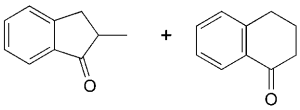
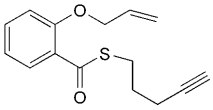
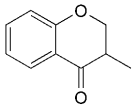
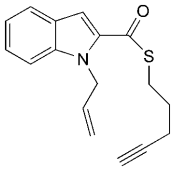
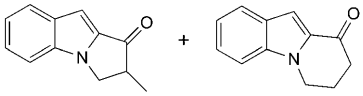
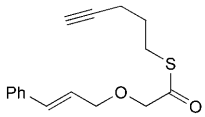
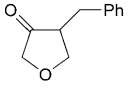
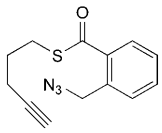
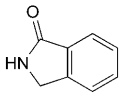
Substrate	Product(s)	Yield [%]
		80
		89
		85
		35
		71

Table 5 (cont.)

Substrate	Product(s)	Yield [%]
		30 + 20
		79
		52 + 16
		83
		70 + 3
		78
		80 + 4
		54
		31

[a]) All reactions were conducted by dropwise addition of thiophenol and AIBN to the substrate in benzene under reflux.

REFERENCES

[1] B. Giese, 'Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds', Pergamon, Oxford, 1986.
[2] W. P. Neumann, *Synthesis* **1987**, 665.
[3] 'C-Radikale: Methoden der Organischen Chemie', Vol. E19a, Eds. B. Giese and M. Regitz, Thieme, Stuttgart, 1989.
[4] C. P. Jasperse, D. P. Curran, T. L. Fevig, *Chem. Rev.* **1991**, *91*, 1237.
[5] D. P. Curran, in 'Comprehensive Organic Synthesis', Vol. 4, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, pp. 715.
[6] D. P. Curran, in 'Comprehensive Organic Synthesis', Vol. 4, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, pp. 779.
[7] W. B. Motherwell, D. Crich, 'Free Radical Chain Reactions in Organic Synthesis', Academic Press, London, 1992.
[8] B. Giese, T. Kopping, T. Göbel, J. Dickhaut, G. Thoma, K. J. Kulicke, F. Trach, *Org. React.* **1996**, *48*, 301.
[9] I. Ryu, N. Sonoda, D. P. Curran, *Chem. Rev.* **1996**, *96*, 177.
[10] 'Radicals in Organic Synthesis', Eds. P. Renaud and M. P. Sibi, Wiley-VCH, Weinheim, 2001.
[11] D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong, N. Curtis, *J. Am. Chem. Soc.* **1980**, *102*, 4438.
[12] A. L. J. Beckwith, P. E. Pigou, *Aust. J. Chem.* **1986**, *39*, 77.
[13] D. P. Curran, C. P. Jasperse, M. J. Totleben, *J. Org. Chem.* **1991**, *56*, 7169.
[14] M. Newcomb, *Tetrahedron* **1993**, *49*, 1151.
[15] C. H. Schiesser, L. M. Wild, *Tetrahedron* **1996**, *52*, 13265.
[16] J. C. Walton, *Acc. Chem. Res.* **1998**, *31*, 99.
[17] A. L. J. Beckwith, K. U. Ingold, in 'Rearrangements in Ground and Excited States', Vol. 1, Ed. P. de Mayo, Academic Press, New York, 1980, pp. 162.
[18] K. U. Ingold, B. P. Roberts, 'Free Radical Substitution Reactions: Biomolecular Homolytic Substitutions at Saturated Multivalent Atoms', Wiley, New York, 1971.
[19] D. Crich, in 'Organosulfur Chemistry: Synthetic Aspects', Vol. 1, Ed. P. Page, Academic Press, London, 1995, pp. 49.
[20] I. Ryu, T. Okuda, K. Nagahara, N. Kambe, M. Komatsu, N. Sonoda, *J. Org. Chem.* **1997**, *62*, 7550.
[21] B. P. Roberts, *Chem. Soc. Rev.* **1999**, *28*, 25.
[22] D. Crich, Q. Yao, *J. Org. Chem.* **1995**, *60*, 84.
[23] D. Crich, X.-Y. Jiao, Q. Yao, J. S. Harwood, *J. Org. Chem.* **1996**, *61*, 2368.
[24] D. Crich, J.-T. Hwang, S. Gastaldi, F. Recupero, D. J. Wink, *J. Org. Chem.* **1999**, *64*, 2877.
[25] J. A. Kampmeier, T. R. Evans, *J. Am. Chem. Soc.* **1966**, *88*, 4096.
[26] J. A. Kampmeier, R. B. Jordan, M. S. Liu, H. Yamanaka, D. J. Bishop, in 'Organic Free Radicals', Ed. W. A. Pryor, ACS Symposium Series, No 69, Washington, 1978, pp. 275.
[27] L. Benati, P. C. Montevecchi, A. Tundo, G. Zanardi, *J. Chem. Soc., Perkin Trans. 1* **1974**, 1272.
[28] A. L. J. Beckwith, S. A. M. Duggan, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1509.
[29] J. A. Franz, D. H. Roberts, K. F. Ferris, *J. Org. Chem.* **1987**, *52*, 2256.
[30] A. L. J. Beckwith, D. R. Boate, *J. Chem. Soc., Chem. Commun.* **1986**, 189.
[31] T. Ooi, M. Furuya, D. Sakai, K. Maruoka, *Adv. Synth. Catal.* **2001**, *343*, 166.
[32] P. C. Van Dort, P. L. Fuchs, *J. Org. Chem.* **1997**, *62*, 7142.
[33] P. C. Van Dort, P. L. Fuchs, *J. Org. Chem.* **1997**, *62*, 7137.
[34] D. Crich, T. K. Hutton, K. Ranganathan, *J. Org. Chem.* **2005**, *70*, 7672.
[35] J. Coulomb, V. Certal, L. Fensterbank, E. Lacôte, M. Malacria, *Angew. Chem., Int. Ed.* **2006**, *45*, 633.
[36] C. Chatgilialoglu, D. Crich, M. Komatsu, I. Ryu, *Chem. Rev.* **1999**, *99*, 1991.
[37] D. Crich, Q. Yao, *J. Org. Chem.* **1996**, *61*, 3566.
[38] D. Crich, D.-H. Suk, X. Hao, *Tetrahedron* **2002**, *58*, 5789.
[39] D. Crich, D.-H. Suk, *Can. J. Chem.* **2004**, *82*, 75.
[40] D. Crich, J.-T. Hwang, H. Yuan, *J. Org. Chem.* **1996**, *61*, 6189.

[41] D. Crich, Q. Yao, *Org. Lett.* **2003**, *5*, 2189.
[42] D. Crich, Q. Yao, *J. Am. Chem. Soc.* **2004**, *126*, 8232.
[43] C. J. Hayes, N. M. A. Herbert, N. M. Harrington-Frost, G. Pattenden, *Org. Biomol. Chem.* **2005**, *3*, 316.
[44] B. De Boeck, N. M. Harrington-Frost, G. Pattenden, *Org. Biomol. Chem.* **2005**, *3*, 340.
[45] L. Benati, R. Leardini, M. Minozzi, D. Nanni, P. Spagnolo, S. Strazzari, G. Zanardi, *Org. Lett.* **2002**, *4*, 3079.
[46] D. Crich, Q. Yao, *Tetrahedron* **1998**, *54*, 305.
[47] B. Giese, X. Beyrich-Graf, J. Burger, C. Kesselheim, M. Senn, T. Schafer, *Angew. Chem., Int. Ed.* **1993**, *32*, 1742.
[48] B. Giese, *Top. Curr. Chem.* **2004**, *236*, 27.
[49] D. Crich, F. Brebion, D.-H. Suk, *Top. Curr. Chem.* **2006**, *263*, 1.
[50] P. A. Baguley, J. C. Walton, *Angew. Chem., Int. Ed*. **1998**, *37*, 3072.
[51] A. Studer, S. Amrein, *Synthesis* **2002**, 835.
[52] D. Crich, X. Hao, *J. Org. Chem.* **1997**, *62*, 5982.
[53] N. Bashir, J. A. Murphy, *Chem. Commun.* **2000**, 627.
[54] L. Benati, G. Calestani, R. Leardini, M. Minozzi, D. Nanni, P. Spagnolo, S. Strazzari, *Org. Lett.* **2003**, *5*, 1313.
[55] L. Benati, R. Leardini, M. Minozzi, D. Nanni, R. Scialpi, P. Spagnolo, G. Zanardi, *Synlett* **2004**, 987.

Received March 23, 2006