3 Reaction Mechanisms
Part (iii) Free-radical Reactions

By STEPHEN CADDICK and KERRY JENKINS
School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK

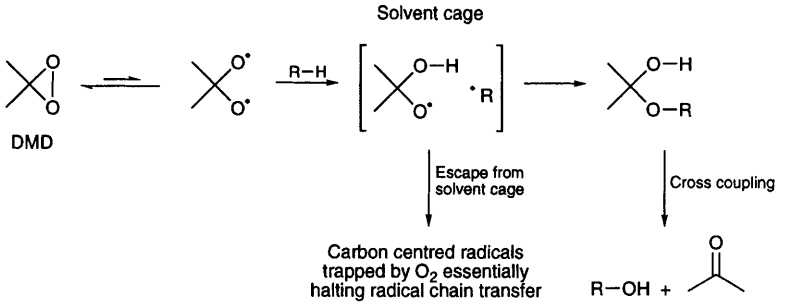
1 Introduction

Contributions to the area of organic free-radicals have been made this year from a wide range of groups including synthetic, physical-organic and bio-organic chemists reflecting the continuing importance of the field. The complex issues surrounding the origin of the β-oxygen effect in Barton deoxygenation reactions are discussed in an illuminating full paper by Crich *et al.*[1] This informative report gives many useful clues to the nature of this well-known but little understood effect; perhaps one of the most important conclusions is that the stabilization of the carbon radical by the β-C–O bond is not significant and that relief of unfavourable dipolar interactions in the transition state is an important feature.

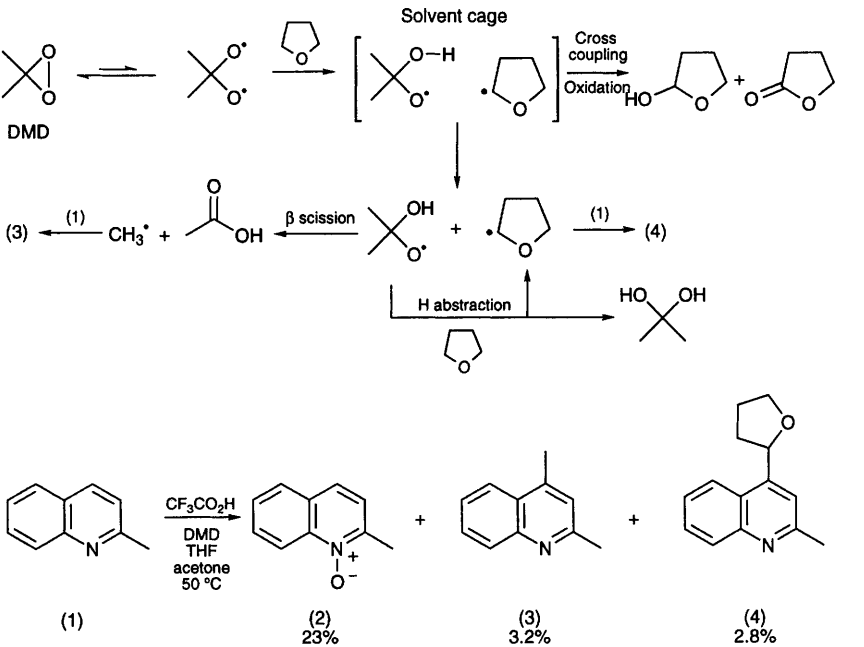
2 Initiators, Promoters, Reagents and Precursors

The oxidation of alkanes continues unsurprisingly to attract considerable attention and the debate regarding radical intermediates in the Gif oxidation continued throughout 1995.[2] In a short but very nice account, Hill describes work carried out by his group in the area of alkane oxidation using polyxometallates based primarily on tungsten.[3] The oxidation of alkanes using the increasingly popular dimethyldioxirane (DMD) has been shown fairly convincingly, by Minisci and collaborators, to proceed *via* a radical based mechanism. They show that the oxidation of alkanes, such as cyclohexane, occurs with greater efficiency in the presence of an oxygen atmosphere and is significantly retarded in the presence of inhibitors such as TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxyl).[4] These exciting results are explained by the authors in a mechanism which involves alkane induced homolysis of the DMD as an initiation process (Scheme 1).

These workers have also reported a similar radical mechanism for the DMD mediated oxidation of a range of functional groups including alkyl and aryl halides,[5] alcohols, aldehydes and ethers. The intermediacy of carbon-centred radicals in the oxidation of some of these functional groups is supported by trapping experiments as



Scheme 1



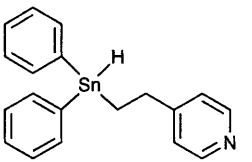
Scheme 2

illustrated by the oxidation of tetrahydrofuran (THF) with subsequent trapping with protonated quinolines[6] (Scheme 2).

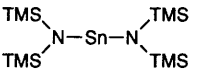
Of course, the use of organic halides as precursors to carbon-centred radicals is a widely used strategy by synthetic organic chemists. A number of interesting reports highlight some alternative reagents which might be used in certain instances to generate carbon radicals from these versatile precursors. For example Negrel and co-workers claim that alkyl bromides will react with lithium aluminium hydride under strictly anaerobic conditions to give carbon-centred radicals[7] and Wayner and

co-workers describe the reduction of bromo esters with pentamethylpiperidine and mercaptoethanol, which is claimed to be radical in nature.[8] Whilst interesting, at present both methods suffer from some practical limitations; however further developments may lead to some synthetically useful and complementary new procedures. More traditionally, group 14 metal hydrides have been used for the transformation of organic halides into carbon radicals, although the associated problems are well-established and require further attention. In this area Clive and Yang have described full details of the preparation of reagent (5) which they use in a range of standard reductive transformations.[9] The yields of these transformations are comparable with those obtained using more conventional tin based reagents but the authors claim that the ease of purification when generating non-polar products is a significant advantage. Chatgilialoglu and Ballestri have reported the use of tris(trimethylsilyl)germane as a reducing agent[10] which is commercially available and is a slightly more effective hydrogen atom donor than tributyltin hydride (TBTH) ($K_{GeH} = 3.1 \times 10^6\,dm^3\,s^{-1}\,mol^{-1}$ at 25 °C). The use of allylstannanes in radical allylation reactions has become a very popular synthetic methodology. However, in order to transfer more elaborate allyl derivatives the availability of the appropriate stannane may become an important issue. In an interesting report Fouquet and co-workers describe their preparation of monoalkylstannanes *via* oxidative addition using the known stannylene (6). The resulting compounds, (7), are of particular interest since they are relatively stable, if protected from water, and will undergo very efficient radical transfer with alkyl radicals generated under 'standard' conditions as described in the paper. From a practical viewpoint it appears that these reagents may have some considerable advantage over more conventional allyltrialkylstannanes in that the displacement reactions proceed with a smaller excess of reagent (1.2 equiv.).[11] In addition, the by-products are sensitive to hydrolysis and the desired products are easier to purify from the 'inorganic' tin residue. Another tin based reagent (8) has been described by Tada and Kaneko[12] and the reagent has been used to effect cyclization under photochemical conditions.

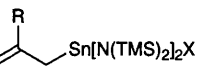
Kraus and co-workers[13] have developed the use of triethylamine, zinc and sub-



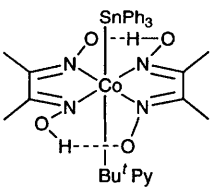
(5)



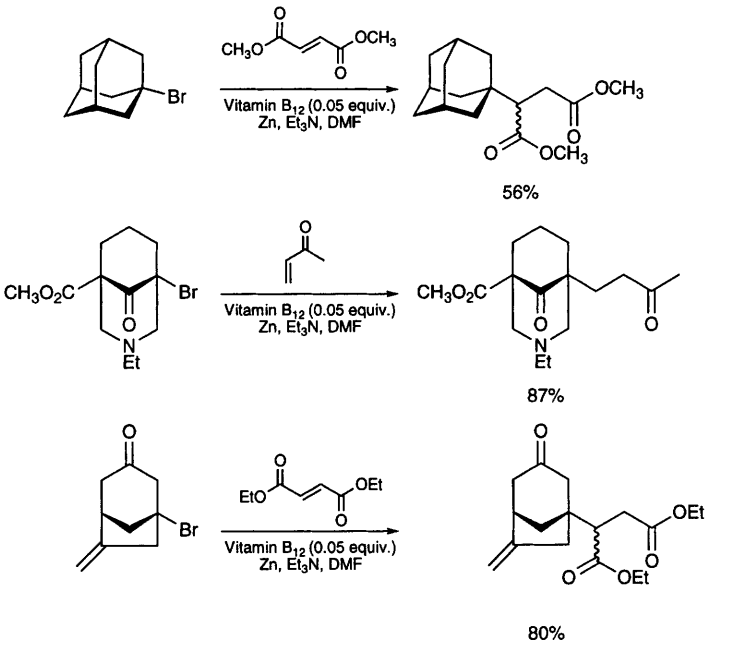
(6)



(7)
X = Cl, Br, I
R = H, Cl, Ph, CN
CO_2Et



(8)



Scheme 3

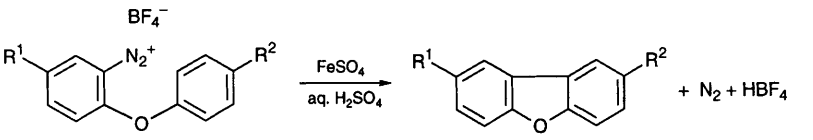
stoichiometric quantities of vitamin B_{12} to effect the generation of bridgehead radicals which then undergo a range of addition reactions as illustrated in Scheme 3.

The use of arenediazonium salts as precursors to aryl radicals is enjoying a revival and, as Murphy and co-workers have shown, tetrathiafulvalene (TTF) is a particularly useful catalyst for this purpose.[14] In this work the aryl radical generated is trapped in a range of addition and substitution reactions. Furthermore, Wassmundt and co-workers have trapped aryl radicals generated from arenediazonium species by addition to other aromatic groups as shown in Scheme 4. They use a variety of methods for generating the intermediate aryl radical, and found that optimal yields were obtained using $FeSO_4$, although there is no mention of the results when TTF is used.[15]

A range of other methods for the generation of carbon radicals have been described. For example, Minisci and co-workers have developed general procedures for intramolecular aromatic substitutions based on copper, silver and iron[16] and systems based on lanthanide/zinc have been used to effect diene cyclizations with perfluorinated alkyl iodides.[17]

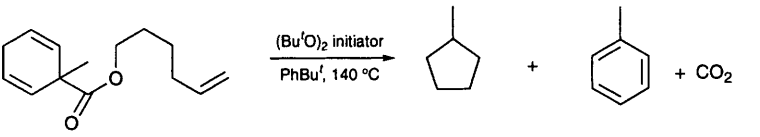
The radical decarboxylation process has long been recognized as a useful method for the generation of carbon-centred radicals and this year two interesting new variants have been reported. One of these, described by Binmore *et al.*,[18] is based on the generation of CO_2 and a stable aromatic by-product and is illustrated in the transformation of (9) to (10) in Scheme 5.

Motherwell and his collaborators have also developed an interesting procedure based on the reaction of *O*-acylthiohydroxamates with thionitrite esters.[19] Thus



R^1	R^2	Yield (%)
H	CH_3	80
H	OCH_3	82
CH_3	CH_3	80
CH_3	H	77
H	H	83
H	Cl	79

Scheme 4



(9) (10)

Scheme 5

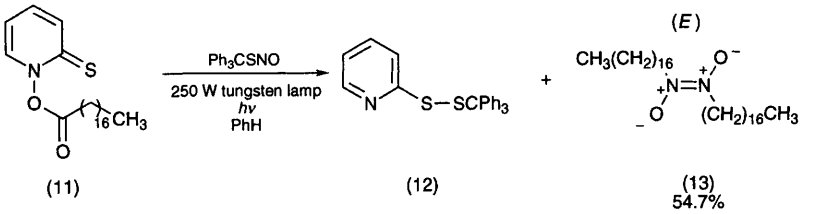
treatment of hydroxamate (11) with trityl thionitrite gives the dimer (13) *via* a chain process involving a substitution reaction, presumably *via* addition–elimination of the alkyl radical to the thionitrite (Scheme 6). The intermediate nitroso species then rapidly dimerizes. These materials can be converted into synthetically useful monomeric species in quantitative yield, by heating in isopropyl alcohol or by catalytic hydrogenation. One of the limitations of the methodology is that it cannot be extended to tertiary carboxylic acids, the authors rationalize this by comparing the ability of primary and secondary nitroso compounds to dimerize with that of tertiary nitroso compounds.

3 Intramolecular Reactions

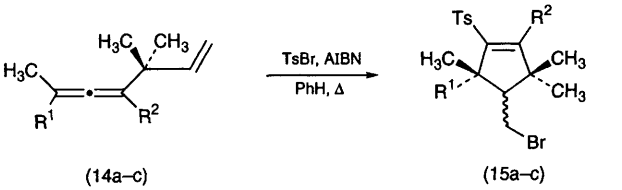
Tosyl radical-mediated additions and/or cyclization reactions have been developed further; Hatem and co-workers show the cyclization of allylallenes (14a–c) to (15a–c) in good yield using tosyl bromide (Scheme 7).[20]

In a synthetic approach to forskolin, Pancrazi and co-workers demonstrated the feasibility of an effective 6-*endo-trig* enyne cyclization as shown in Scheme 8.[21]

The generation and cyclization of indol-2-yl radicals has been reported by Jones and collaborators.[22] The generation and manipulation of 2-halo-indoles enables the preparation of the precursors which then undergo smooth cyclization (Scheme 9). This approach nicely demonstrates an alternative to most of the known radical methods for making C–C bonds at the 2 position of indoles.

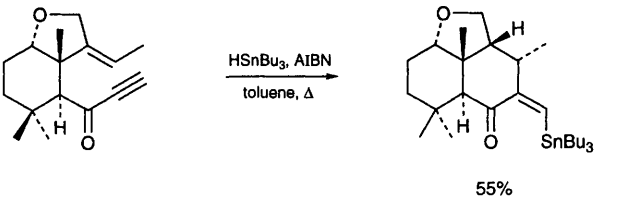


Scheme 6



	R^1	R^2	Yield (%)
a	CH_3	H	82
b	H	H	24 *cis*/17 *trans*
c	H	Et	53 *cis*/29 *trans*

Scheme 7

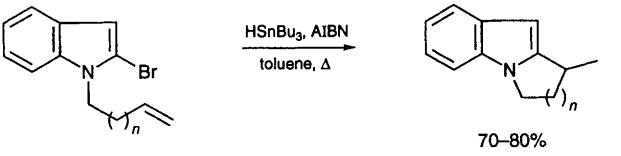


Scheme 8

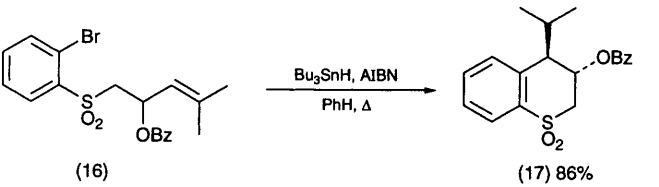
Translocations

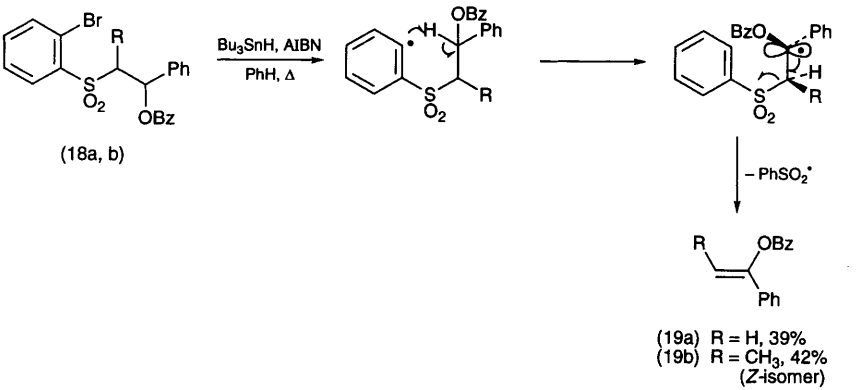
Simpkins and co-workers have explored the possibility of developing a radical based alkene synthesis involving a radical abstraction followed by β-scission.[23] Somewhat surprisingly they found that the abstraction process was fairly slow and in a competition experiment found that cyclization was the preferred reaction. For example, when (16) was treated with TBTH cyclization products, *e.g.* (17), were isolated in reasonable yields (Scheme 10). The only examples in which the alkene synthesis was successful utilized precursors in which cyclization was not possible, *e.g.* in the transformation of (18a) or (18b) to (19a) or (19b).

The use of organosilanes as hydrogen atom donors in translocation reactions has been put to good use in controlling reactivity. Thus Clive and Cantin[24] have cleverly exploited the propensity of silicon containing precursors to confer *endo*-selectivity in a



Scheme 9

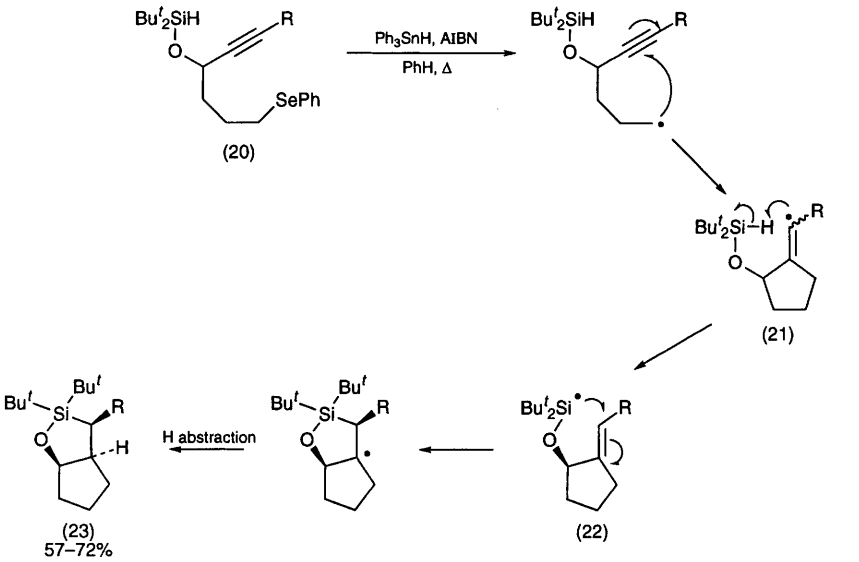




Scheme 10

very elegant sequence as illustrated in the transformation of (20) to (23) in Scheme 11. The first cyclization proceeds to generate the intermediate vinyl radical species (21) and thence the silicon centred radical (22) which then undergoes 5-*endo-trig* cyclization. The siloxane products are amenable to further synthetic manipulation as detailed in the paper.

Curran and co-workers have also utilized efficient hydrogen-atom transfer from silanes to assist in mediating 'slow' bimolecular radical processes.[25] As shown in Scheme 12, addition of the radical derived from bromide (24) is very inefficient and either low yields of mixtures or large recovery of starting alkene results from more conventional reaction conditions. However, simply modifying the silyl protecting groups as in substrate (26) results in an efficient addition process which, after deprotection gives product (29) in good yield with only 5 mol% ditin required (Scheme 12). The propagating steps here involve fast intramolecular hydrogen atom transfer



Scheme 11

[(27) to (28)] and intermolecular bromine atom transfer which is slow. This cleverly designed process should have significant practical applications.

Aromatics

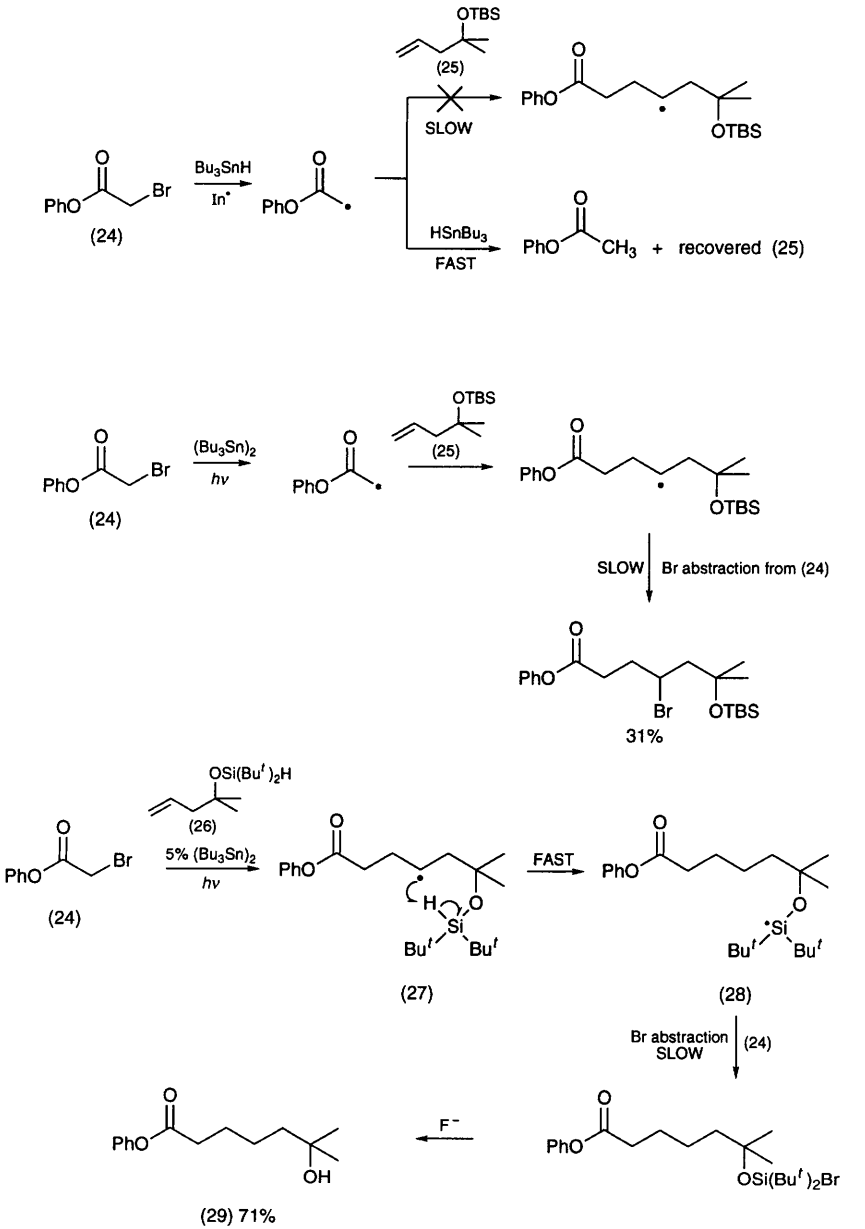
Jones and co-workers have shown that aryl radicals can add to pyrrole nuclei as exemplified in the transformation of (30a–c) to (31a–c) (Scheme 13).[26]

Aromatic Substitution

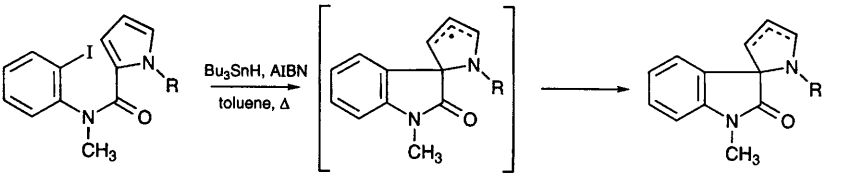
Minisci and co-workers have shown that intramolecular carbamoylation of heteroaromatics *via* ipso substitution can be achieved.[27] Addition of alkyl radicals to a range of heteroaromatics has been reported by Chuang and Wang as highlighted in the transformation of (32) to (33) using sodium toluene-*p*-sulfinate (TsNa) in the presence or absence of $Cu(OAc)_2$ (Scheme 14).[28]

Substitution at the 2-position of indoles can provide a useful method for the synthesis of functionalized and fused indoles. Two different approaches have been reported. The first involves the direct H-atom substitution which may, in view of previous work by Ziegler, be dependent upon the presence of substituents at the 3-position.[29] The second involves phenylthio and phenylsulfinyl substitution, but takes place without substitution at the 3-position (Scheme 15).[30]

Beckwith and Storey have very elegantly promoted aromatic ipso substitution but have incorporated a H-atom transfer step in the sequence.[31] Thus oxindoles (35a) and (35b) result from treatment of aryl bromides (34a) and (34b) with TBTH–$(Bu^tO)_2$ (Scheme 16).



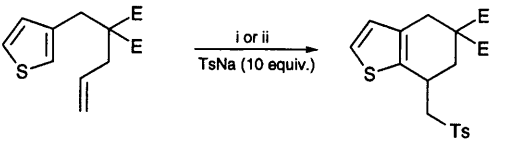
Scheme 12



(30a–c) a, R = CH_3
b, R = H
c, R = CO_2Bu^t

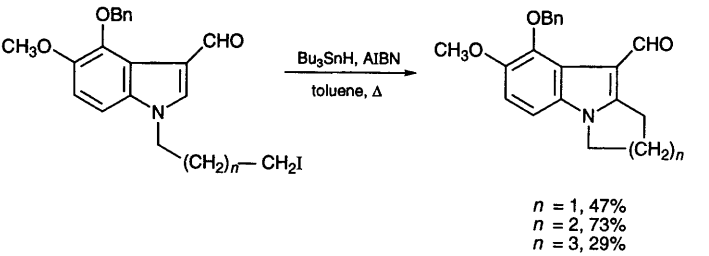
(31a–c) a, 28%
b, 34%
c, 12%

Scheme 13

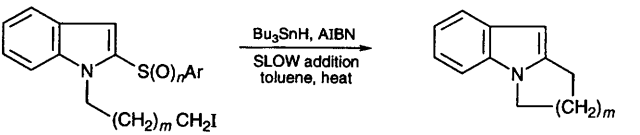


(32) (33)

Scheme 14 *Reagents and conditions*: i, heat, 48 h, 66%; ii, $Cu(OAc)_2$ (2 equiv.), heat, 24 h, 81%



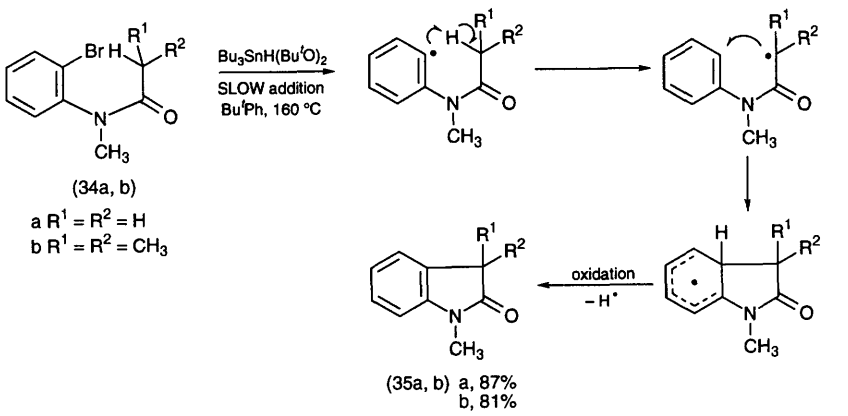
n = 1, 47%
n = 2, 73%
n = 3, 29%



n = 0, *m* = 1, 24%
n = 0, *m* = 2, 50%

n = 1, *m* = 1, 40%
n = 1, *m* = 2, 50%
n = 1, *m* = 3, 30%

Scheme 15



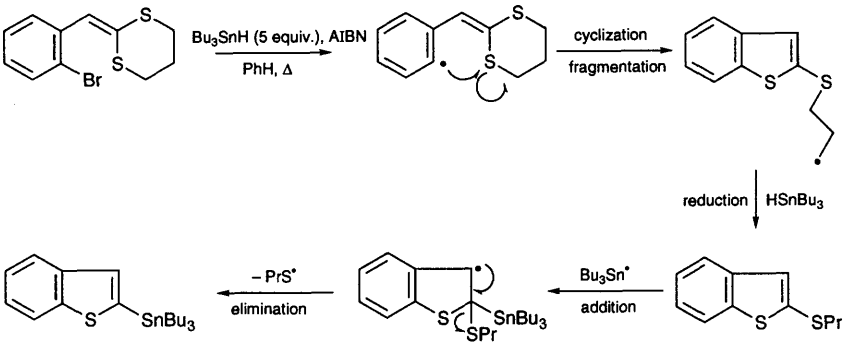
(34a, b)

a $R^1 = R^2 = H$

b $R^1 = R^2 = CH_3$

(35a, b) a, 87%
b, 81%

Scheme 16



(36) 70%

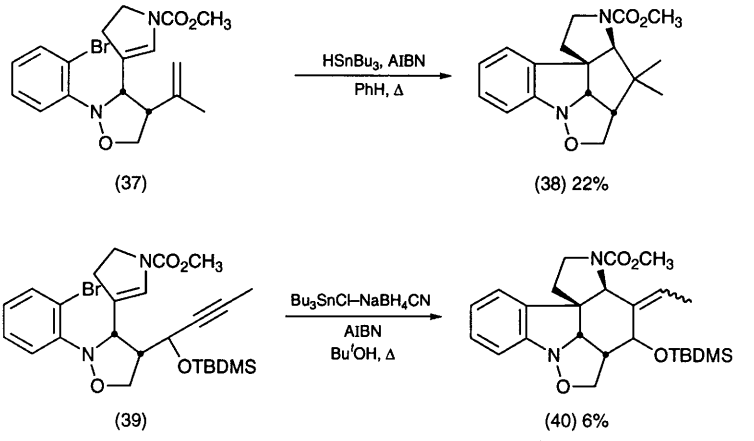
Scheme 17

Cascade/Tandem Reactions

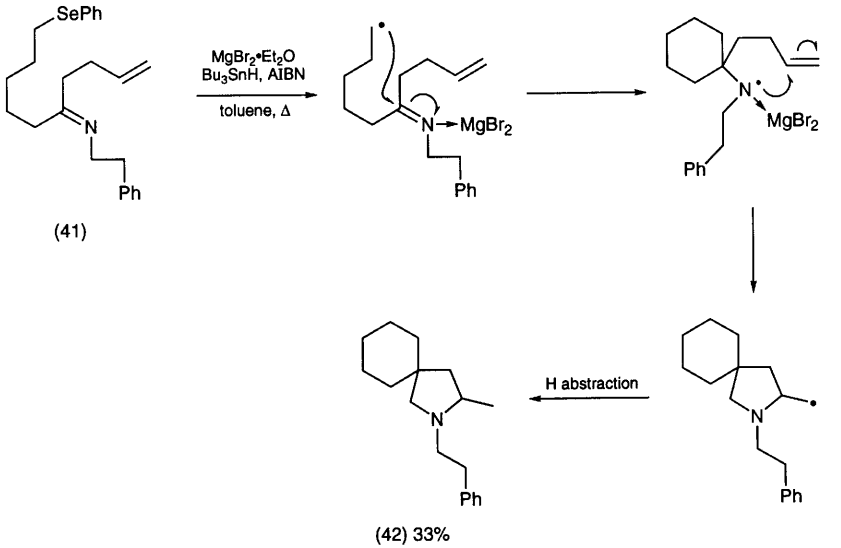
In a very elegant and efficient example of a tandem process Harrowven and Browne have developed an approach to condensed thiophenes as shown in Scheme 17.[32] This sequence involves an unusual cyclization–fragmentation sequence which after reduction undergoes intermolecular ipso substitution to give the tributylstannyl substituted benzothiophene (36) in good yield.

Parsons and co-workers have examined some complex but appealing tandem cyclization reactions toward pseudocopsinine and aspidosperma alkaloids as shown in the transformation of (37) to (38) and (39) to (40) respectively (Scheme 18).[33]

Bowman *et al.* have developed an approach to heterocyclic bicycles *via* tandem cyclization involving addition of an alkyl radical to an imine followed by addition of the nitrogen centred radical to an alkene. The use of a Lewis acid ($MgBr_2 \cdot Et_2O$) assists the cyclization of the aminyl radical intermediate and generally results in improved



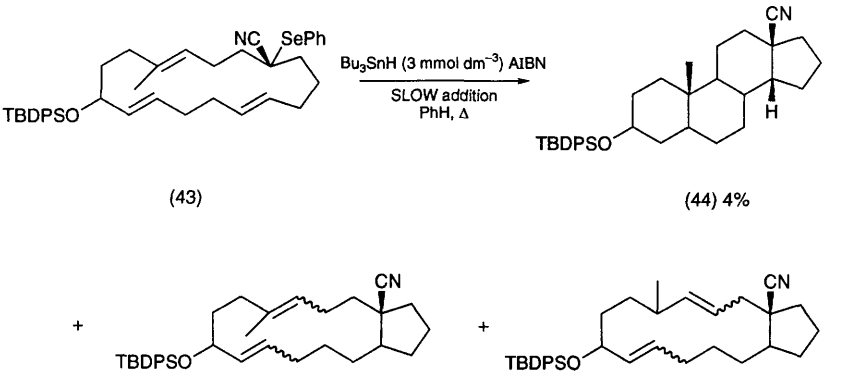
Scheme 18



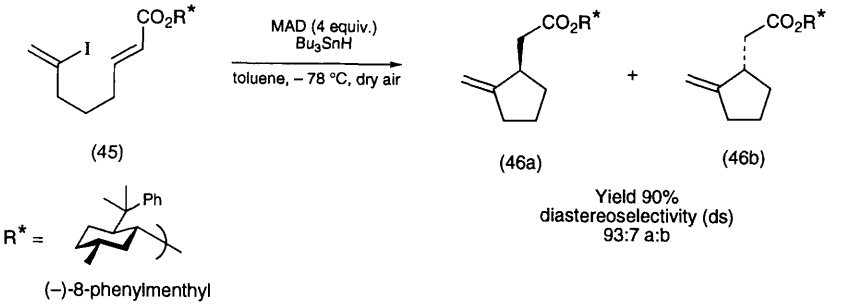
Scheme 19

yields as highlighted in the cyclization of (41) to (42) in Scheme 19.[34]

Jahn and Curran have reported a rapid but low yielding tandem cyclization approach to the steroid skeleton as shown in the transformation of (43) to (44) (Scheme 20). The poor yield of this process is attributed, with experimental verification, to the more favourable translocation processes which can intervene.[35]



Scheme 20

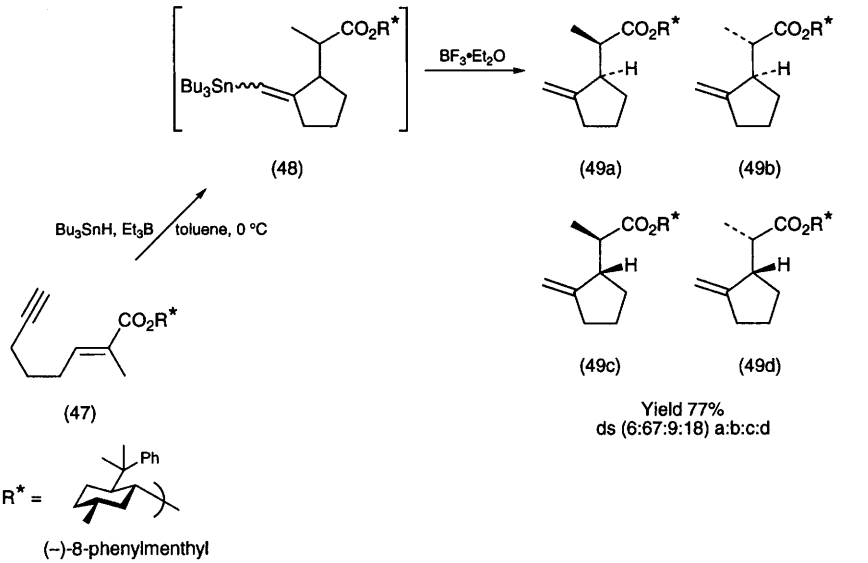


Scheme 21

Stereoselectivity

Stereoselective cyclizations are of great importance particularly in natural product synthesis and Ishibashi and co-workers have shown that using a matched pair of auxiliaries can lead to good stereoselectivity in asymmetric radical reactions.[36] Nishida and co-workers have, in a series of investigations, illustrated that good levels of stereoselectivity can be achieved in the cyclization of vinyl radicals onto electron deficient alkenes bearing chiral auxiliaries. These workers show the importance of the nature of the Lewis acid, particularly in view of the fact that in certain instances the Lewis acid appears to negate the use of a conventional initiator (*e.g.* Et_3B) as shown in the transformation of (45) to (46a) and (46b) (Scheme 21);[37] at present it is unclear whether this is a general feature of this type of cyclization.[38]

Reactions of this type are clearly quite complex and a more detailed understanding is essential prior to developing more general synthetic procedures. It would appear however that the Lewis acid simply enhances the levels of stereoselectivity in cyclizations of this type which can still proceed with fairly good levels of stereocontrol without Lewis acid as shown in the cyclization of (47) to (49a–d) (Scheme 22).[39]



Scheme 22

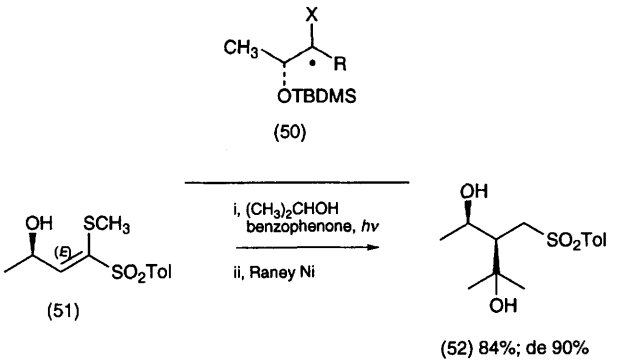
4 Intermolecular Reactions

Further important contributions in this area have been made this year.[40,41] In the general field of substrate control, Giese continues to probe 1,2-stereoinduction and is attempting to derive some general rules regarding the stereochemical outcome for radicals of the general structure (50). He concludes that if X is a conjugating planar group then the A-strain model can be used to rationalize stereochemical outcome. If the substituent is linear or tetrahedral stereoinduction is negligible and if X is oxygen then the stereochemical outcome can be rationalized using the Felkin–Anh rule.[42,43]

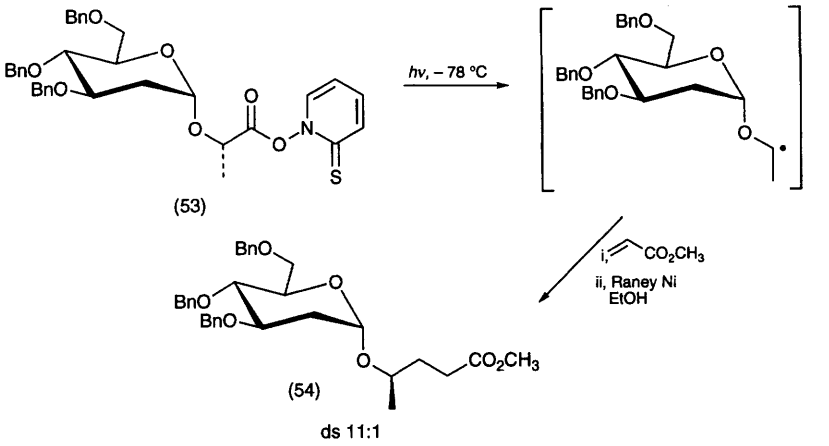
The problems associated with attempting to predict the stereochemical outcome of substrate-controlled reactions are made clear, once again by Giese, in the continuing developments in enolate radicals which have been shown to be sensitive to polar effects, unless one of the substituents is extremely bulky.[44] Guindon has examined similar systems which have yielded good levels of stereocontrol which can be reversed using Lewis acids.[45]

Ogura and co-workers describe a system in which high 1,2-*syn*-selectivity can be achieved as illustrated in the transformation of (51) to (52)[46] (Scheme 23) and Taguchi and co-workers have examined stereoselective radical additions to γ-oxy-α,β-unsaturated esters in cyclic and acyclic systems.[47]

Auxiliaries continue to attract considerable attention. Garner and co-workers have utilized carbohydrates as recoverable auxiliaries for use in diastereoselective radical addition reactions as shown in the formation of (54) from (53)[48] (Scheme 24) and Hamon and co-workers detail, in full, some of their investigations into asymmetric radical additions of glycine derivatives.[49]



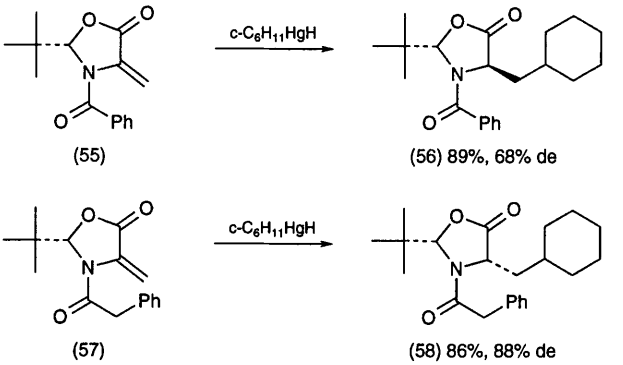
Scheme 23



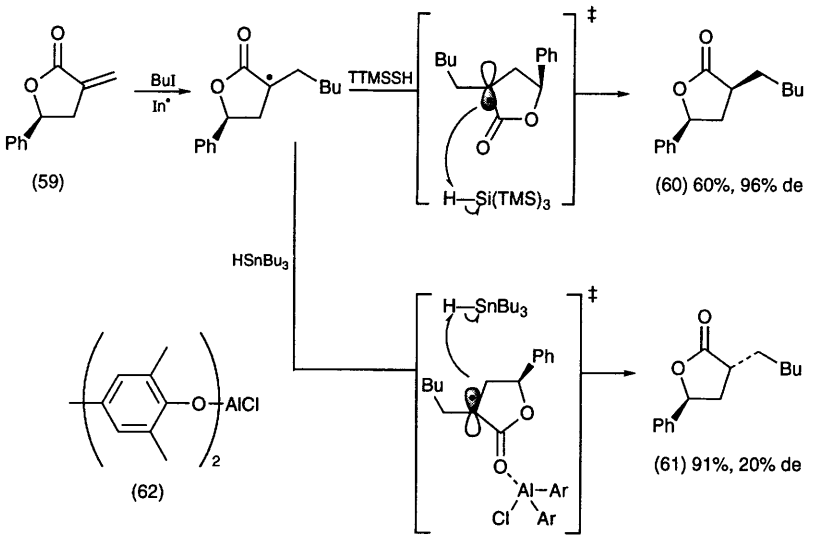
Scheme 24

Axon and Beckwith have developed a very practical and versatile approach to either enantiomer of α-amino acids utilizing oxazolidinones.[50] They exploit a very useful protecting group effect to prepare either enantiomer of a particular series; thus treatment of (55) or (57) with cyclohexyl radical leads to the 'pseudo' epimeric products (56) and (58) with good levels of stereocontrol (Scheme 25). Hydrogenolysis leads to the free amino acid. The ability to prepare either enantiomer by modifying the protecting group bodes well for the practical application of this strategy.

Sato and co-workers have also used a diastereoselective approach to prepare carboxylic acid derivatives and are also able to prepare either epimeric product, in this case by modifying the reaction conditions.[51] They find that addition of alkyl radical to acceptor (59) using the appropriate hydrogen atom donor [in this case tris(trimethylsilyl)silane (TTMSSH) is optimal] leads to the product in which the hydrogen atom donor approaches from the least hindered face as shown. The selectivity can be reversed



Scheme 25

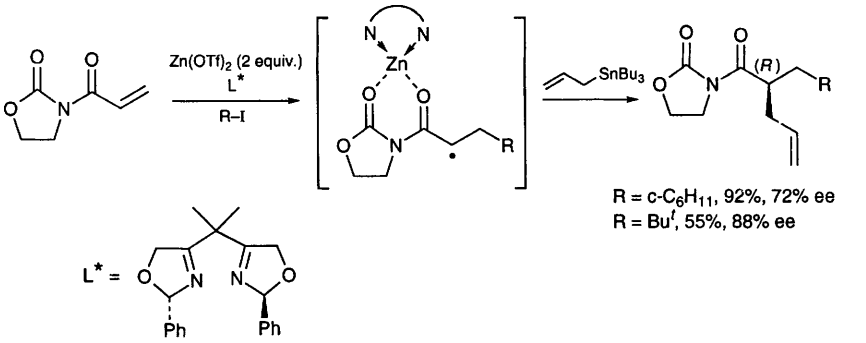


Scheme 26

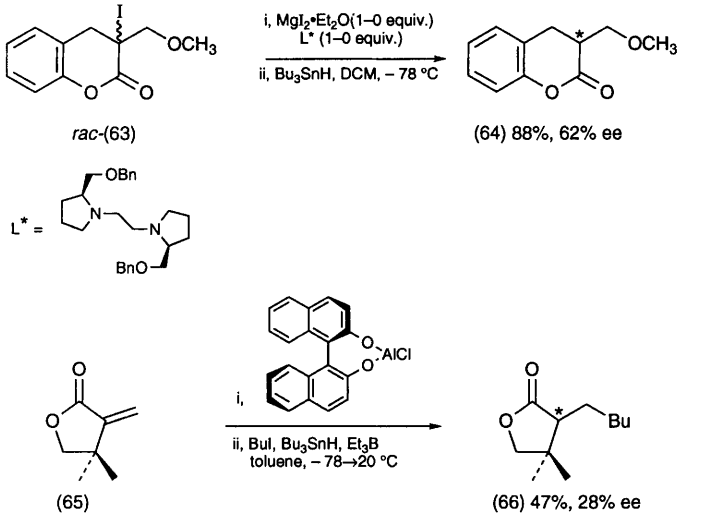
by carrying out the reaction in the presence of a bulky Lewis acid, such as (62), which coordinates to the carbonyl from the least hindered face, forcing the hydrogen atom donor to approach from the opposite face to give predominantly the epimeric product (61).

The use of achiral auxiliaries as templates for chiral, non-racemic promoters is an interesting and valuable strategy for asymmetric synthesis and Porter and co-workers have applied this approach to effect relative[52] and absolute[53] stereocontrol in radical addition reactions as shown in Scheme 27.

Hoshino and co-workers have used an enantioselective halide reduction using a



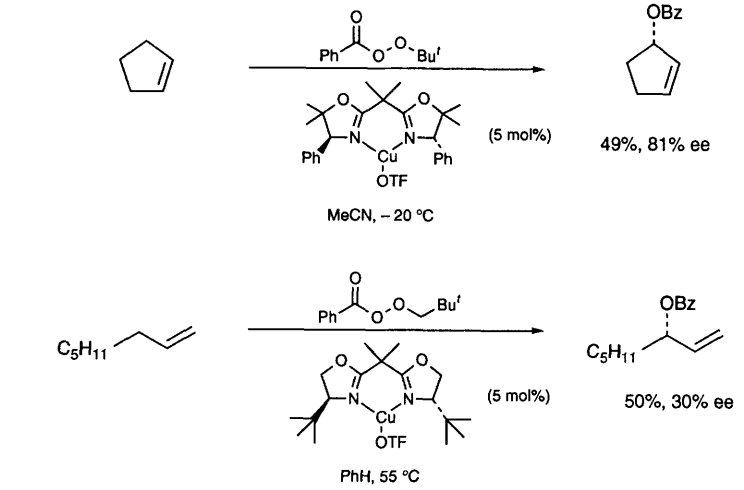
Scheme 27



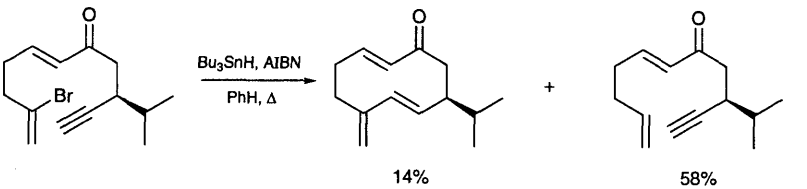
Scheme 28

magnesium based system with good yields and promising ees [see reaction of (63) to (64), Scheme 28].[54] Subsequently, the use of a chiral, non-racemic aluminium based Lewis acid to effect a similar asymmetric hydrogen atom transfer to an enolate radical has also been reported by Sato and co-workers[55] illustrated in the transformation of (65) to (66). Although the levels of enantioselectivity are moderate, these are exciting developments in the area.

The asymmetric oxidation of alkanes is of course one of the most fundamental types of transformation one can achieve in organic chemistry and Andrus and co-workers exploit the ubiquitous copper–bis-oxazoline systems to effect catalytic enantioselective allylic oxidation with modest yields but promising levels of enantioselectivity (40–60% yield, up to 80% ee) as shown in Scheme 29.[56]



Scheme 29



Scheme 30

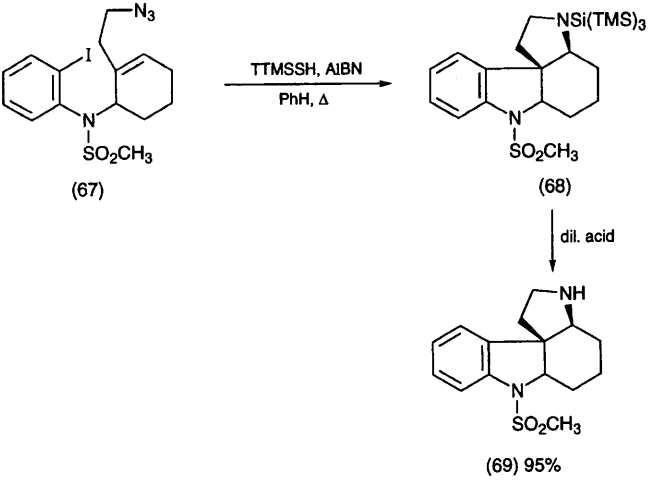
5 Applications to Natural Product Synthesis

Parsons *et al.* have developed an elegant synthesis of the sensitive cyclodecene core common to the periplanone class of insect attractant *via* a 10-*endo-dig* cyclization as shown in Scheme 30.[57]

In an approach to the aspidosperma class of alkaloids Kizil and Murphy have developed an azide terminated tandem cyclization of (67) to (68) and thence (69) (Scheme 31).[58]

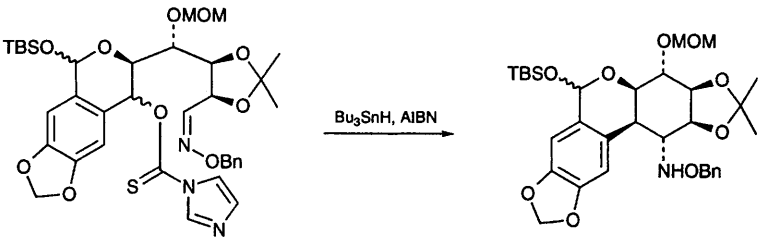
The synthesis of (+)-7-deoxypancratistatin by Keck and co-workers incorporates a radical cyclization of thiocarbonylimidazole precursor (70) to (71) in good yield (Scheme 32).[59]

Finally this section would not be complete without mention of the transannular cyclization strategy toward 7,8-epoxybasmen-6-one described in full by Myers and Condroski and this strategy is highlighted in Scheme 33.[60]



(67) (68) (69) 95%

Scheme 31

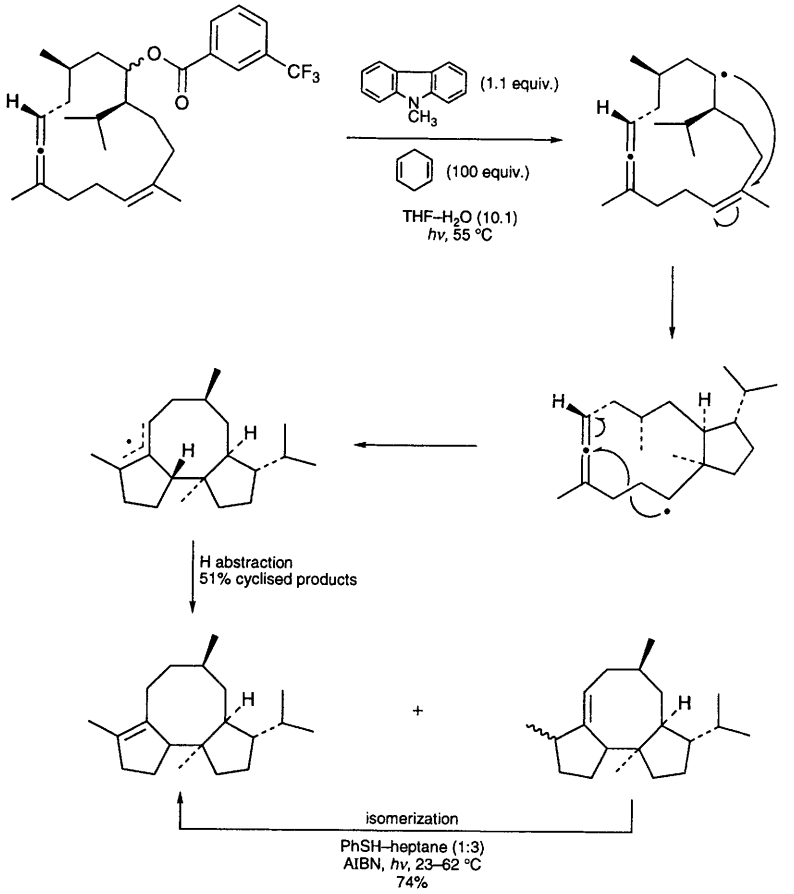


(70) (71) 70%

Scheme 32

References

1 D. Crich, A. L. J. Beckwith, C. Chen, Q. Yak, I. G. E. Davison, R. W. Longmore, C. Anaya de Parrodi, L. Quintero-Cortes and J. Sandoval-Ramirez, *J. Am. Chem. Soc.*, 1995, **117**, 8757.
2 F. Minisci, F. Fontana, S. Araneo, F. Recupero, S. Banfi and S. Quici, *J. Am. Chem. Soc.*, 1995, **117**, 226.
3 C. L. Hill, *Synlett*, 1995, 127.
4 A. Bravo, F. Fontana, G. Fronza, A. Mele and F. Minisci, *J. Chem. Soc., Chem. Commun.*, 1995, 1573.
5 A. Bravo, F. Fontana, G. Fronza, F. Minisci and A. Serri, *Tetrahedron Lett.*, 1995, **36**, 6945.
6 F. Minisci, L. Zhao, F. Fontana and A. Bravo, *Tetrahedron Lett.*, 1995, **36**, 1895.
7 E. Peralez, J.-C. Negrel and M. Chanon, *Tetrahedron Lett.*, 1995, **36**, 6457.
8 M. Amoli, M. S. Workentin and D. D. M. Wayner, *Tetrahedron Lett.*, 1995, **36**, 3997.
9 D. L. J. Clive and W. Yang, *J. Org. Chem.*, 1995, **60**, 2607.
10 C. Chatgilialoglu and M. Ballestri, *Organometallics*, 1995, **14**, 5017.
11 E. Fouquet, M. Pereyre and T. Roulet, *J. Chem. Soc., Chem. Commun.*, 1995, 2387.
12 M. Tada and K. Kaneko, *J. Org. Chem.*, 1995, **60**, 6635.
13 G. A. Kraus, T. M. Siclovan and B. Watson, *Synlett*, 1995, 201.
14 R. Fletcher, C. Lampard, J. A. Murphy and N. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1995, 623.



Scheme 33

15 F.W. Wassmundt and R. Pedemonte, *J. Org. Chem.*, 1995, **60**, 4991.
16 S. Araneo, F. Fontana, F. Minisci, F. Recupero and A. Serri, *Tetrahedron Lett.*, 1995, **36**, 4307.
17 W.-Y. Huang, G. Zhao and Y. Ding, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1729.
18 G. Binmore, J.C. Walton and L. Cardellini, *J. Chem. Soc., Chem. Commun.*, 1995, 27.
19 P. Girard, N. Guillot, W.B. Motherwell and P. Potier, *J. Chem. Soc., Chem. Commun.*, 1995, 2385.
20 F. El Gueddari, J.R. Grimaldi and J.M. Hatem, *Tetrahedron Lett.*, 1995, **36**, 6685.
21 C. Ames, L. Billot, J. Lallemand and A. Pancrazi, *Tetrahedron Lett.*, 1995, **36**, 7247.
22 A.P. Dobbs, K. Jones and K.T. Veal, *Tetrahedron Lett.*, 1995, **36**, 4857.
23 C.D.S. Brown, A.P. Dishington, O. Shishkin and N.S. Simpkins, *Synlett*, 1995, 943.
24 D.L.J. Clive and M. Cantin, *J. Chem. Soc., Chem. Commun.*, 1995, 319.
25 D.P. Curran, J. Xu and E. Lazzarini, *J. Am. Chem. Soc.*, 1995, **117**, 6603.
26 K. Jones, T.C.T. Ho and J. Wilkinson, 36, 6743.
27 F. Minisci, F. Fontana, F. Coppa and Y.M. Yan, *J. Org. Chem.*, 1995, **60**, 5430.
28 C.-P. Chuang and S.-F. Wang, *Synlett*, 1995, 763.
29 C.J. Moody and C.L. Norton, *Tetrahedron Lett.*, 1995, **36**, 9051.
30 S. Caddick, K. Aboutayab, R. West, *J. Chem. Soc., Chem. Commun.*, 1995, 1353.
31 A.L.J. Beckwith and J.M.D. Storey, *J. Chem. Soc., Chem. Commun.*, 1995, 977.

32 D.C. Harrowven and R. Browne, *Tetrahedron Lett.*, 1995, **36**, 2861.
33 P.J. Parsons, C. P. Penkett, M. C. Cramp, R. I. West, J. C. Warrington and M. C. Saraiva, *Synlett*, 1995, 507.
34 W. R. Bowman, P. T. Stephenson and A. R. Young, *Tetrahedron Lett.*, 1995, **36**, 5623.
35 U. Jahn and D. P. Curran, *Tetrahedron Lett.*, 1995, **36**, 8921.
36 H. Ishibashi, C. Kameoka, K. Kodama and M. Ikeda, *Synlett*, 1995, 915.
37 M. Nishida, H. Hayashi, O. Yonemitsu, A. Nishida and N. Kawahara, *Synlett*, 1995, 1045.
38 M. Nishida, H. Hayashi, Y. Yamaura, E. Yanaginuma, O. Yonemitsu, A. Nishida and N. Kawahara, *Tetrahedron Lett.*, 1995, **36**, 269.
39 M. Nishida, M. Nobuta, K. Nakaoka, A. Nishida and N. Kawahara, *Tetrahedron: Asymmetry*, 1995, 2657.
40 D. P. Curran and L. Balas, *Synlett*, 1995, 119.
41 H. Urabe, K. Yamashita, K. Suzuki, K. Kobayashi and F. Sato, *J. Org. Chem.*, 1995, **60**, 3576.
42 B. Giese, M. Bulliard, J. Dichau, R. Halbach, C. Hassler, U. Hoffmann, B. Hinzen and M. Senn, *Synlett*, 1995, 116.
43 P. Renaud and M. Gerster, *J. Am. Chem. Soc.*, 1995, **117**, 6607.
44 C. Hassler, R. Batra and B. Giese, *Tetrahedron Lett.*, 1995, **36**, 7639.
45 Y. Guindon, B. Guerin, C. Chabot, N. Mackintosh and W. W. Ogilvie, *Synlett*, 1995, 449.
46 K. Ogura, A. Kayano, N. Sumitani, M. Akazome and M. Fujita, *J. Org. Chem.*, 1995, **60**, 1106.
47 T. Morikawa, Y. Washio, S. Harada, R. Hanai, T. Kayashita, H. Nemoto, M. Shiro and T. Taguchi, *J. Chem. Soc., Perkin Trans.* 1, 1995, 271.
48 P. P. Garner, P. B. Cox and S. J. Klippenstein, *J. Am. Chem. Soc.*, 1995, **117**, 4183.
49 D. P. G. Hamon, R. A. Massy-Westropp and P. Razzino, *Tetrahedron*, 1995, **51**, 4183.
50 J. R. Axon and A. L. J. Beckwith, *J. Chem. Soc., Chem. Commun.*, 1995, 549.
51 H. Urabe, K. Kobayashi and F. Sato, *J. Chem. Soc., Chem. Commun.*, 1995, 1043.
52 R. Radinov, C. L. Mero, A. T. McPhail and N. A. Porter, *Tetrahedron Lett.*, 1995, **36**, 8183.
53 J. H. Wu, R. Radinov and N. A. Porter, *J. Am. Chem. Soc.*, 1995, **117**, 11029.
54 M. Murakata, H. Tsutsui and O. Hoshino, *J. Chem. Soc., Chem. Commun.*, 1995, 481.
55 H. Urabe, K. Yamashita, K. Suzuki, K. Kobayashi and F. Sato, *J. Am. Chem. Soc.*, 1995, **60**, 3576.
56 M. Andrus, A. B. Argade, X. Chen and M. G. Pamment, *Tetrahedron Lett.*, 1995, **36**, 2945.
57 D. Jonas, Y. Ozlu and P. J. Parsons, *Synlett*, 1995, 255.
58 M. Kizil and J. A. Murphy, *J. Chem. Soc., Chem. Commun.*, 1995, 1409.
59 G. E. Keck, S. F. McHardy and J. A. Murry, *J. Am. Chem. Soc.*, 1995, **117**, 7289.
60 A. G. Myers and K. R. Condroski, *J. Am. Chem. Soc.*, 1995, **117**, 3057.