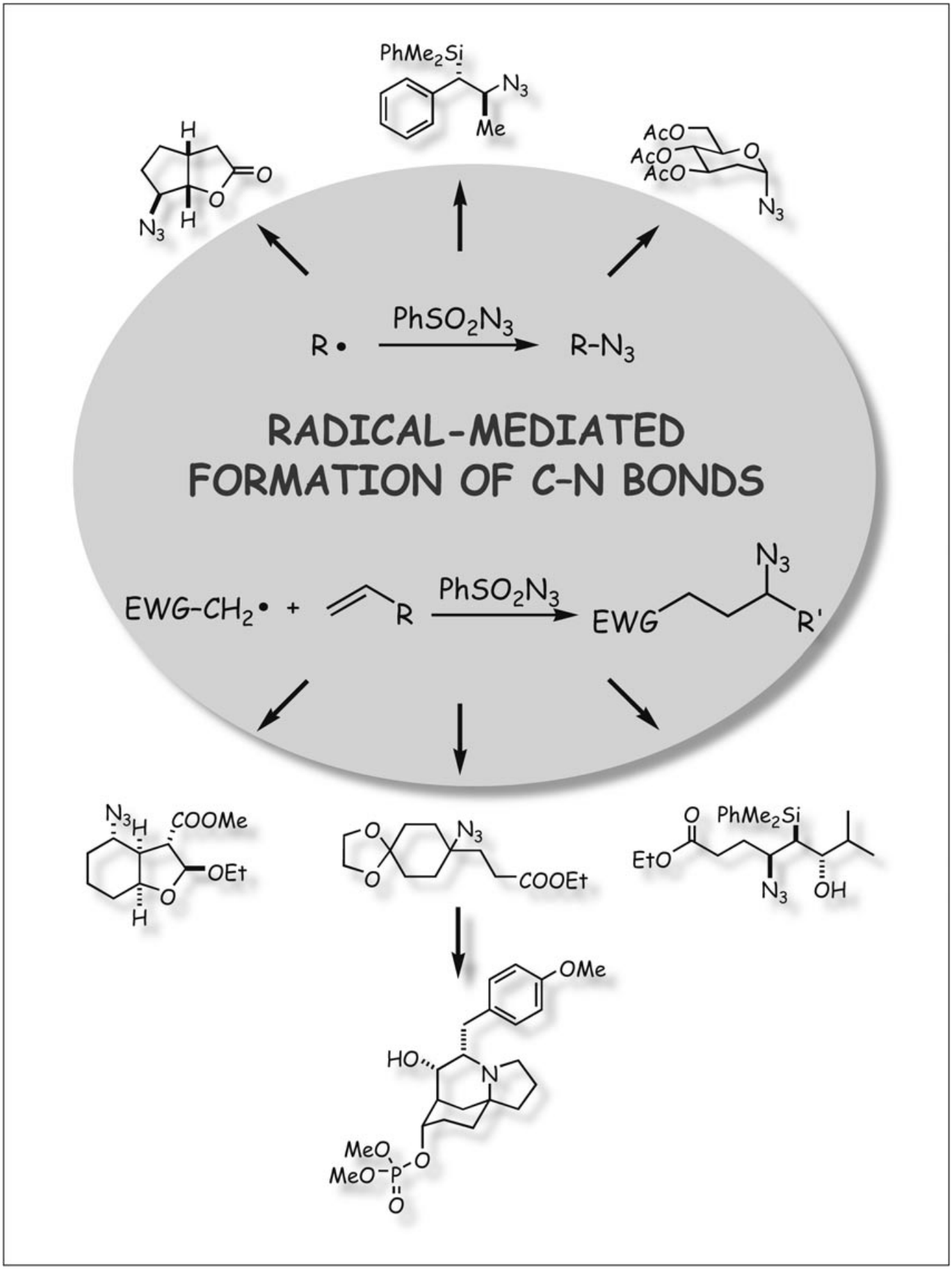

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Radical Amination with Sulfonyl Azides: A Powerful Method for the Formation of C–N Bonds

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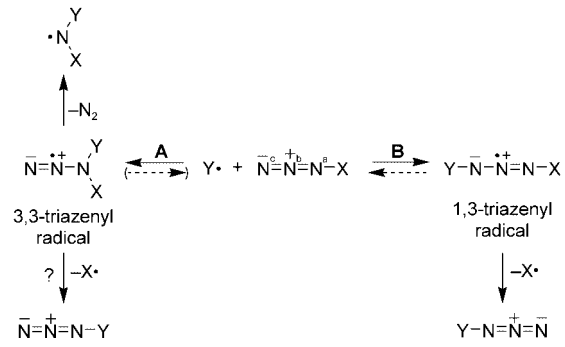
Abstract: A novel reaction for the introduction of an azide moiety by means of a mild radical process is currently under development. Sulfonyl azides are suitable azidating agents for nucleophilic radicals, such as secondary and tertiary alkyl radicals. More electrophilic radicals, such as enolate radicals, do not react with sulfonyl azides. This feature allowed the development of efficient intra- and intermolecular carboazidations of olefins. Due to the versatility of the azido group, this reaction has an important synthetic potential, as already demonstrated by the preparation of the core of several alkaloids, particularly those containing an amino-substituted quaternary carbon center, such as FR901483.

Keywords: alkaloids · amination · azides · radical reactions · synthetic methods

Introduction

The use of free-radical reactions in multistep synthesis has steadily increased over the last years, mainly because of their compatibility with a large number of functional groups and their high potential for performing sequential transformations.[1] A lot of effort has been concentrated on the development of chain reactions for the formation of carbon–carbon bonds under reducing (Giese reaction)[2] or atom transfer (Kharasch–Curran)[3,4] conditions. Formation of carbon–nitrogen bonds by means of a radical pathway is highly attractive for the synthesis of alkaloids and related heterocyclic compounds. Most of the effort reported in this field deals with the addition of nitrogen-centered radicals to olefins.[5,6] The reverse process, that is, addition of a carbon-centered radical to a nitrogen-containing trap is much less developed, despite the fact that nitrosation of cyclohexane is a classical textbook example of an industrial radical reaction. The use of nitric oxide (often generated from nitrite ester), azo derivatives, and imines has been reported with very variable success.[7,8] Organic azides of type $X–N_3$ have also been investigated as radical traps. They can undergo homolytic addition at either the inner (N^a, path A) or the terminal (N^c, path B) nitrogen atom to give a 3,3-triazenyl or a 1,3-triazenyl radical, respectively (Scheme 1).[9,10] The



Scheme 1. Possible reactions of organic azides with radicals.

3,3-triazenyl radical (path A) evolves presumably by rapid loss of nitrogen to furnish an aminyl radical. Fragmentation of X• to deliver the azide $Y–N_3$ cannot be excluded. On the other hand, the 1,3-triazenyl radical (path B) may fragment

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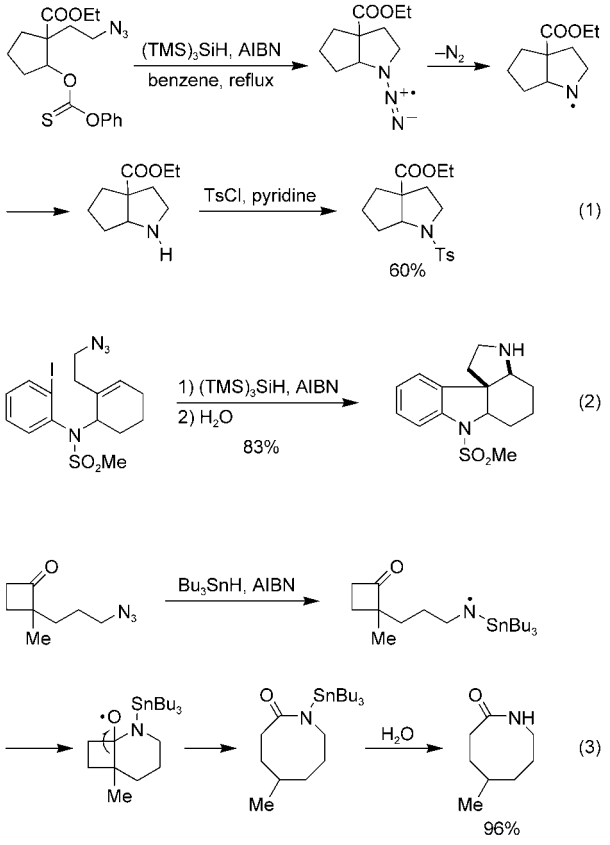
to liberate the radical $X^{\bullet}$ and $Y{-}N_3$. This last reaction corresponds to an azidation of the radical $Y^{\bullet}$.

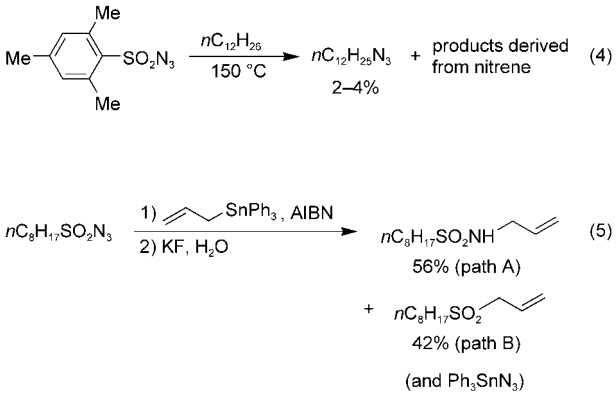
Azides as Radical Trap

Kim reported efficient radical cyclizations involving azides as radical traps [Scheme 2, Eq. (1)].[11] This intramolecular amination process is efficient and proceeds via a 3,3-triazenyl radical that readily eliminates nitrogen to afford an aminyl radical. This reaction found several applications in the total synthesis of natural products, such as Murphy's synthesis of aspidospermidine [Scheme 2, Eq. (2)].[12,13] In both examples, reactions occur exclusively according to path A, since they correspond to favorable 5-*exo* cyclization processes. The intermolecular addition of tin radicals onto alkyl azides has also been reported[14] and represents an interesting approach for the generation of aminyl radicals [Scheme 2, Eq. (3)].[15,16] The absence of product resulting from path B can be explained by the reversibility of the addition of the tin radical at N^c and by the lack of fragmentation leading to an alkyl radical (X = primary alkyl group).



Scheme 2. Reaction via aminyl radicals generated through path A in Scheme 1.

In an early experiment, Abramovitch and Breslow observed the formation of traces of alkyl azides during a Curtius type rearrangement of sulfonyl azides.[17–19] This formation was rationalized by a direct reaction between alkyl radicals and sulfonyl azides. A typical example is presented in Equation (4) (Scheme 3). Roberts examined the reaction of aryl and alkyl sulfonyl azides with allylstannanes in order to develop an homolytic allylation reaction at nitrogen [Scheme 3, Eq. (5)].[20] In this reaction, the formation of allylsulfones and stannyl azides represents the major side products. These products arise from the addition of the tin radical at the terminal nitrogen atom followed by fragmentation of a sulfonyl radical.

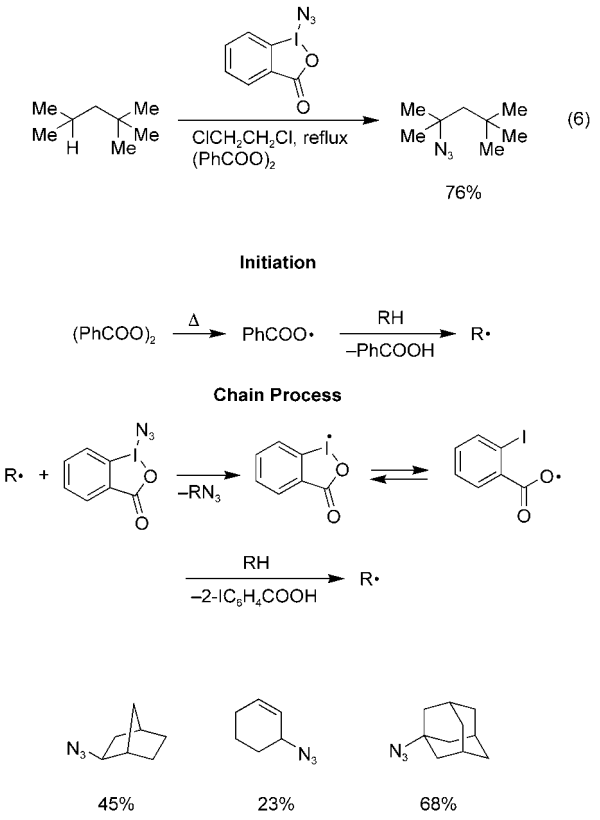


Scheme 3. Early examples of azidation according to path B in Scheme 1.

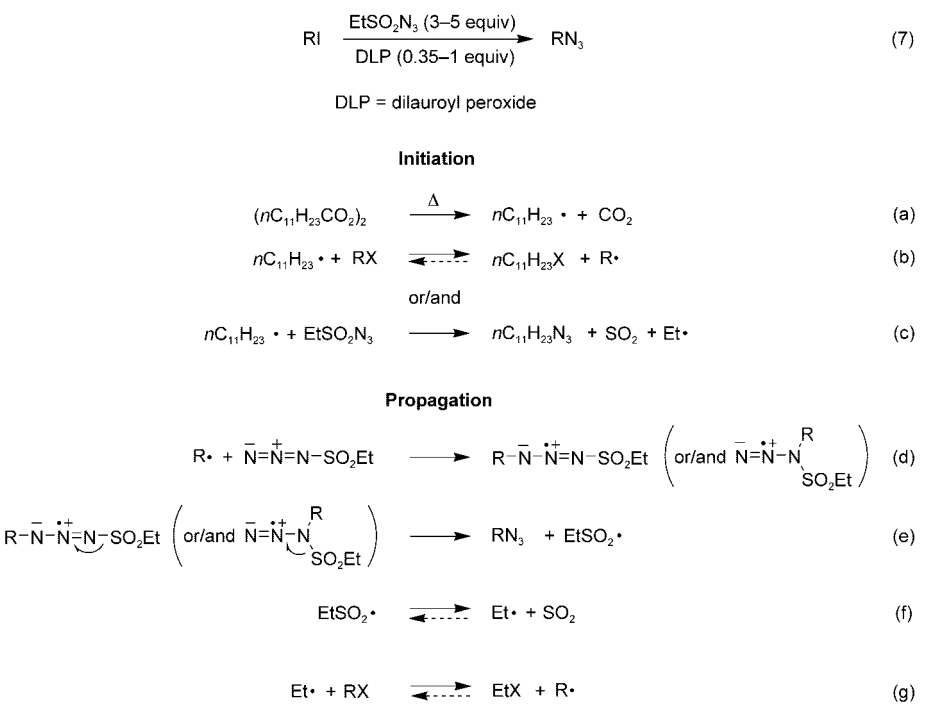
Finally, Zhdankin reported the preparation of stable azidoiodinanes.[21] These compounds proved to be good azidating agents toward various organic substrates and they can be used for direct azidation of hydrocarbons at high temperature and in the presence of radical initiators. For example, 2,2,4-trimethylpentane reacts with 1-azido-1,2-benziodoxole-3-(1*H*)-one in refluxing 1,2-dichloroethane (b.p. 83 °C) in the presence of benzoylperoxide to afford the corresponding azide in 76 % yield [Scheme 4, Eq. (6)]. The proposed mechanism involves hydrogen atom abstraction by the 2-iodobenzoyl radical followed by azidation of the alkyl radical by the azidoiodinane. This elegant chain process proceeds with moderate to good yields at the secondary and tertiary positions of several different alkanes (see Scheme 4).

Radical Azidation with Ethanesulfonyl Azide

Recently, Zard, Fuchs, and Kim reported the formation of carbon–carbon bonds involving the fragmentation of ethane-, methane- and trifluoromethanesulfonyl radicals as the key step.[22–25] These procedures are either based on iodine and xanthate transfers from ethyl and methyl radicals or hydrogen-atom transfers from trifluoromethyl radicals. Based on a similar concept, we envisaged developing an intermolecular radical azidation process of iodides and dithiocarbonates using ethanesulfonyl azide as reagent [Scheme 5, Eq. (7)].[26,27] Ethanesulfonyl azide, easily prepared from ethanesulfonyl chloride and sodium azide, is a stable liquid that can be heated at 100 °C without decomposition. However, since sulfonyl azides are capable of exploding, it is strongly recommended to apply standard safety rules and to use a safety shield. The crucial step of this process is the ad-



Scheme 4. Zhdankin reaction.

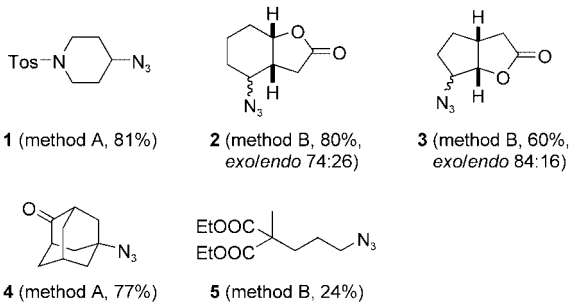


Scheme 5. Radical azidation with ethanesulfonyl azide.

dition of the alkyl radical at the *N*-terminal position of the azido moiety to give a 1,3-triazenyl radical [Scheme 5, Eq. (d)] that fragments to liberate the corresponding alkyl azide and the ethanesulfonyl radical [Scheme 5, Eq. (e)]. This mechanism corresponds to the pathway B depicted in Scheme 1. Addition of the radical at the inner position (path A, Scheme 1) followed by fragmentation of the sulfonyl radical cannot be totally excluded at the moment, but this path should lead to sulfonamide derivatives (not observed) through nitrogen elimination. After sulfur dioxide extrusion [Scheme 5, Eq. (f)], the ethyl radical can propagate the chain by an atom or group transfer process [Scheme 5, Eq. (g)]. The initiation step is a crucial point for the success of the reaction. Early studies with cyclohexyl iodide and azobisisobutyronitrile (AIBN) failed to give the desired azidation product, presumably due to the stability (no iodine atom transfer with cyclohexyl iodide) and the lack of nucleophilicity (no reaction with ethanesulfonyl azide) of the 2-cyanoprop-2-yl radical generated from AIBN. Therefore, an initiator that gives nucleophilic radicals, such as dilauroyl peroxide (DLP), which has been used with much success by Zard in reactions involving iodides and dithiocarbonates[28] and more recently by us for iodine atom transfers,[29] is a perfect candidate to perform such transformations. The undecyl radical delivered by DLP [Scheme 5, Eq. (a)] is expected to react with the radical precursor to initiate the chain reaction [Scheme 5, Eq. (b)]. Reaction of the undecyl radical with ethanesulfonyl azide is also possible [Scheme 5, Eq. (c)]. Small amounts of undecyl azide were isolated at several occasions, confirming this hypothesis.

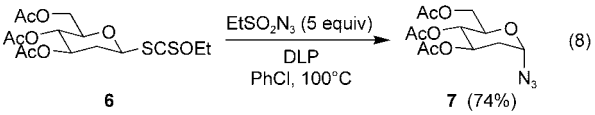
The radical azidation with ethanesulfonyl azide and DLP works well with a variety of secondary and tertiary alkyl iodides (see Scheme 6 for typical examples). The azidation was carried out with three equivalents of ethanesulfonyl azide and a substoichiometric amount of DLP in a refluxing mixture of chlorobenzene and heptane (method A) or, in more difficult cases, with five equivalents of ethanesulfonyl azide in chlorobenzene at 100 °C (method B). Primary alkyl iodides are not efficiently converted into azides (see compound **5**). This inefficiency is caused by the nearly thermoneutral iodine-atom transfer between the ethyl radical and the primary alkyl iodide [Scheme 5, Eq. (g)] as well as by the lower nucleophilicity of primary alkyl radicals relative to secondary and tertiary ones. It is of interest to mention that the classical ionic substitution reaction of the iodolactone precursor of **3** with sodium azide failed to give an azide.

Xanthates are also suitable precursors for radical group transfer reactions. The anomeric xanthate **6**, easily obtained by the nucleophilic substitution of α-bromo-2-desoxyglucose



Scheme 6. Radical azidation of alkyl iodides according to Equation (7).

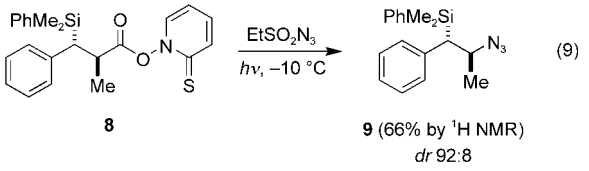
derivative with the commercially available potassium *O*-ethyl xanthate, gives the anomeric azide **7** as a single α-anomer in 74% yield (Scheme 7). Interestingly, the prepara-



Scheme 7. Radical azidation of xanthates according to Equation (7).

tion of such α-anomeric azides is much more difficult than the β-isomers when classical nucleophilic substitution approaches are employed.[30] Moreover, these anomeric azides are useful intermediates for the preparation of biologically important *N*-linked glycoconjugates.

Recently, Porter reported the first decarboxylative azidation of thiohydroxamates (Barton esters).[31] Moderate to good yields of the desired azides were obtained together with the *S*-pyridyl derivatives resulting from the direct trapping of the radical by the Barton ester. Interestingly, these reactions proved to be diastereoselective, as demonstrated by the example depicted in Scheme 8. This point will be further discussed later.

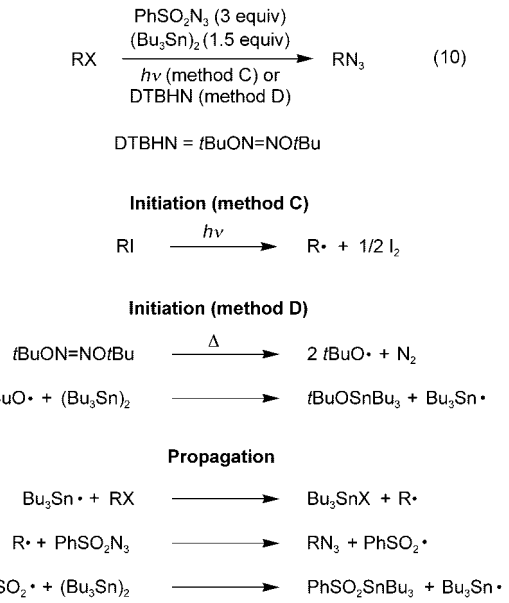


Scheme 8. The decarboxylative azidation reaction.

The azidation of carbon-centered radicals with ethanesulfonyl azide is an attractive tin-free procedure. However, we notice that the purification of the final azides may be problematic when they are apolar. Indeed, they are contaminated with other apolar side products derived from DLP, such as undecyl azide. Furthermore, long reaction times (=12 h) are often necessary for completion of the azidation, due to the relative inefficiency of the chain process. Finally, different attempts to achieve cascade reactions involving radical cyclization and azidation processes in a one-pot procedure failed. Therefore, we decided to look for an alternative azidation procedure that could solve some of these drawbacks.

Ditin-Mediated Radical Azidation with Benzenesulfonyl Azide

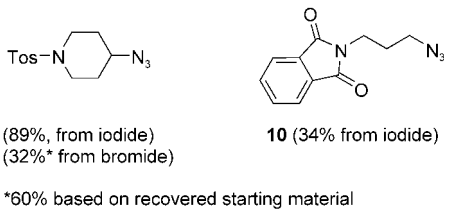
The reaction of ditin derivatives with sulfonyl radicals affords stannyl radicals that can ideally sustain a chain reaction. Moreover, ditin derivatives are inert towards alkyl radicals and no competing reaction, such as the direct reduction of the intermediate alkyl radical, is expected. Therefore, we decided to replace ethanesulfonyl azide by benzenesulfonyl azide and to use hexabutylditin as the chain transfer reagent.[27] Because of the instability of the phenyl radical, the intermediate benzenesulfonyl radical does not loose SO_2. The proposed chain reaction is described in Scheme 9



Scheme 9. Radical azidation with benzenesulfonyl azide.

[Eq. (10)]. The initiation of this process is critical: when alkyl iodides are used as radical precursors, the reaction can be initiated by irradiation with a 300 W sun lamp (method C). However, thermal initiation (80 °C) with di-*tert*-butylhyponitrite (DTBHN) (method D) proved to be more effective. The efficacy of this approach is due to the well-documented reaction of *tert*-butoxyl radicals with hexabutylditin.

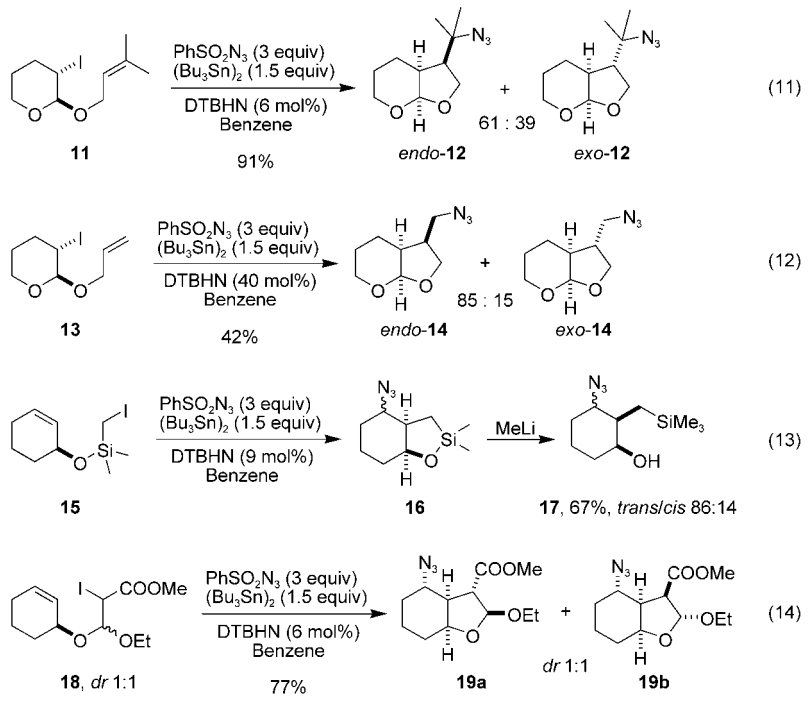
The scope and limitation of this approach has been studied for different radical precursors according to Equation (10) and typical results are summarized in Scheme 10.[27] The azide **1** was prepared from the corresponding iodide in 89% yield by treatment with three equivalents of benzenesulfonyl azide and 1.5 equivalents of hexa-



Scheme 10. Radical azidation according to Equation (10).

butylditin in benzene. Interestingly, under these reaction conditions, the reaction is clean and fast (=4 h) and the purification of the product is easier than in the tin-free procedure described above. The same azide **1** was prepared in 32% yield (60% after correction for recovered starting material) from the corresponding bromide. The primary azide **10** was isolated in a modest 34% yield from its corresponding iodide. This result indicates that the addition of primary alkyl radicals to sulfonyl azide is less efficient than the reaction of the more nucleophilic secondary and tertiary alkyl radicals.

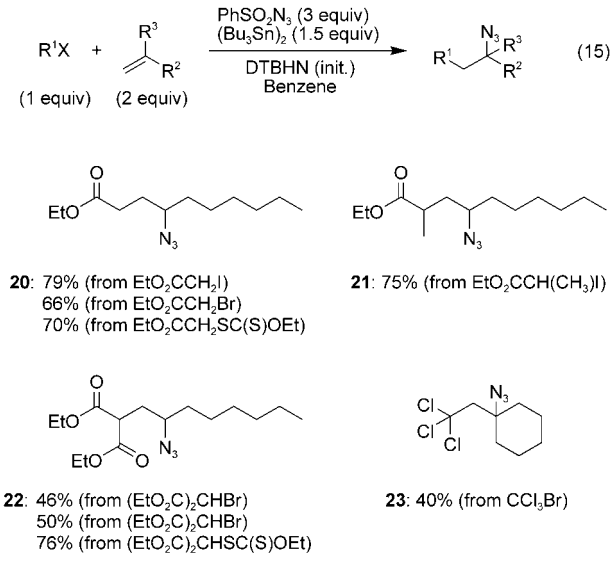
This last point is further supported by the cyclization reaction depicted in Equations (11) and (12) (Scheme 11). The iodoacetal **11** provides the corresponding tertiary azide **12** in 91% yield as a mixture of diastereoisomers (*endo*/*exo* 61:39) [Eq. (11)]. Under similar conditions, the iodoacetal **13** gave the primary azide **14** (*endo*/*exo* 85:15) in 42% yield [Eq. (12)]. The primary (iodomethyl)dimethylsilyl ether **15** is also a suitable precursor for such cyclization–azidation process [Scheme 11, Eq. (13)]. The unstable cyclic silyl ether **16** is immediately converted by treatment with MeLi into the cylcohexanol derivative **17** in 67% overall yield (*trans*/*cis* 86:14). Finally, we have also demonstrated that treatment of the α-iodoacetate **18** (*dr* 1:1) with benzenesulfonyl azide (3 equiv), hexabutylditin (1.5 equiv) and DTBHN as a radical initiator affords the bicyclic azide **19** in 77% yield in a one-pot procedure [Eq. (14)]. Remarkably, each diastereomer of **18** gives a completely diastereoselective reaction.



Scheme 11. Radical cyclization-azidation processes.

The Carboazidation Reaction

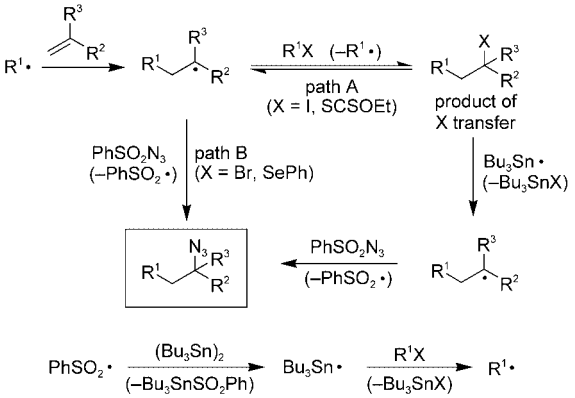
The chemistry depicted in Scheme 11 involves the intramolecular formation of a C–C bond (a radical cyclization) followed by intermolecular C–N bond formation. In all these reactions, no product of direct azidation of the initial radical before cyclization was observed. This encouraged us to examine a process involving two intermolecular reactions. The intermolecular addition of carbon-centered radicals to unactivated alkenes followed by azidation represents a formal carboazidation of alkenes. The feasibility of the reaction was tested with terminal alkenes and different radical precursors that are known to be efficient in radical atom or group transfer reactions [Scheme 12, Eq. (15)]. A one-pot procedure similar to the one used for intramolecular reactions gave promising results: the radical precursors were treated with terminal olefins (2 equiv), benzenesulfonyl azide (3 equiv), hexabutyldistannane (1.5 equiv) and DTBHN (6–18 mol%) as initiator in refluxing benzene.[32,33] Slow addition of benzenesulfonyl azide was not necessary because this electrophilic reagent does not react with the initial electrophilic or ambiphilic radicals, such as enolate radicals and the trichloromethyl radical. Typical examples are reported in Scheme 12. Excellent results were obtained with α-iodo and α-xanthate esters. α-Bromoacetate gives also satisfactory results; however, bromomalonate, phenylseleono-



Scheme 12. The carboazidation of terminal alkenes.

malonate and bromotrichloromethane give lower yields of carboazidation. This is due to the formation of atom or group transfer products that are not efficiently converted into the desired azides under these reaction conditions.

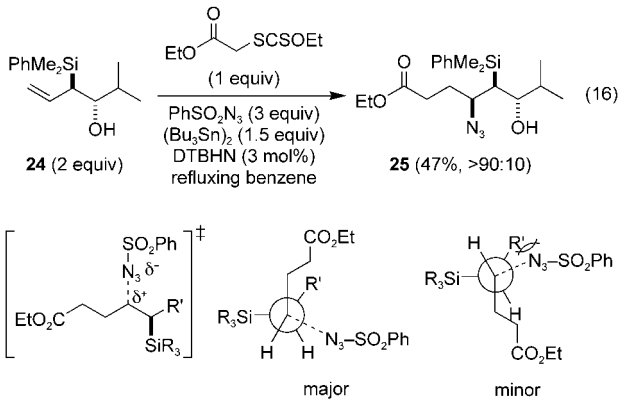
Two reaction pathways (Scheme 13, paths A and B) can operate in the carboazidation of olefins. Path A is a stepwise mechanism involving formation of an intermediate through



Scheme 13. Proposed mechanism.

the transfer of the X group. This pathway is operative when the atom or group transfer is fast. For instance, iodides and xanthates react along this pathway and both steps, that is, carbon–carbon bond formation through atom/group transfer and azidation of the intermediate iodide/xanthate are efficient. The second pathway, path B, is a direct radical addition–azidation process that takes place when the atom transfer step is slower than the azidation step. Bromides activated by a single ester group are expected to follow this reaction pathway. For instance, with ethyl 2-bromoacetate, no product of bromine-atom transfer was detected during the reaction and the overall yield was good. With more activated bromides and selenides, such as diethyl bromomalonate, diethyl phenylselenomalonate, and bromotrichloromethane, the atom/group-transfer process is accelerated and path A becomes again operative. The desired carboazidation products, isolated in moderate yields only, presumably result from a competing direct azidation reaction according to path B, since the intermediate bromides/selenides formed are not efficiently azidated under these reaction conditions.

The control of the stereochemistry of the azidation step in acyclic systems was shown to be possible by using chiral allylsilanes as substrates for the carboazidation process.[34] A typical example is shown in Scheme 14. The allylsilane **24** was converted to **25** with an excellent level of stereochemistry for such a nonstabilized radical intermediate. It was postulated that, as bonding between the radical center and the sulfonyl azide develops, a partial positive charge would appear at the carbon atom due to the high electrophilicity of the radical trap, and this partial positive charge is best stabilized by a coplanar electron rich C–Si bond (silicon β-effect). Based on two assumptions (pyramidalized staggered transition state and silicon β-effect), we propose the models depicted in Scheme 14 to explain the stereochemical outcome of the carboazidation of chiral allylsilanes. These two

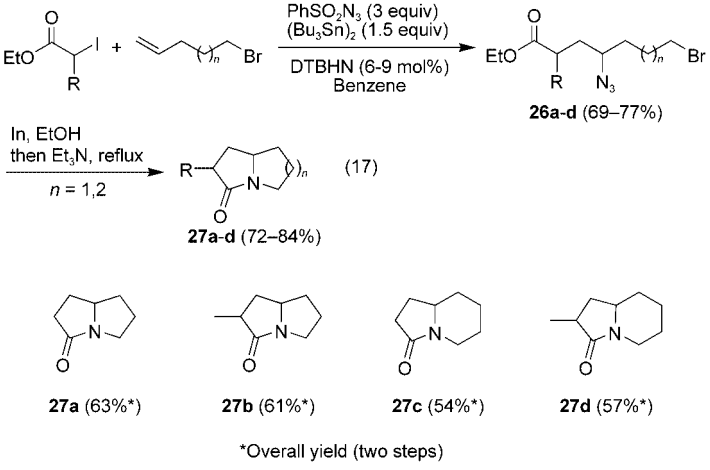


Scheme 14. Stereoselective carboazidation of allylsilanes.

models are characterized by: 1) a quasi staggered transition state, 2) the orthogonal relationship between the bulky silyl group and the $CH_2CH_2CO_2Et$ substituent at the radical center, and 3) the formation of a C–N bond nearly *anti* to the silyl group.

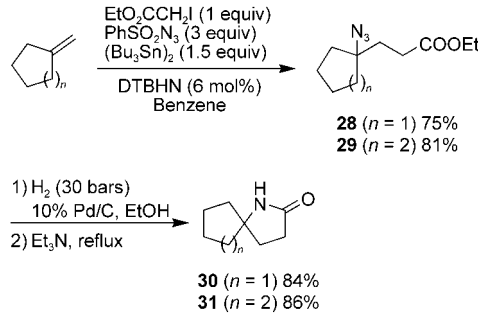
Synthetic Applications

Based on the carboazidation process, efficient three-component syntheses of simple lactams, such as pyrrolidinones, pyrrolizidinones, and indolizidinones can be performed.[32,33] The radical carboazidation of alkenes with 2-iodoesters can be coupled with the reduction of azides to afford 3-amino esters that cyclize to pyrrolidinones. Even more interesting, the carboazidation of 5-bromopent-1-ene and 6-bromocyclohex-1-ene with ethyl 2-iodoacetate and ethyl 2-iodopropionate affords the azido esters **26a–d**, which give, after reduction with indium and treatment with triethylamine, the pyrrolizidinones and indolizidinones **27a–d** by means of a double cyclization reaction [Scheme 15, Eq. (17)]. This reaction sequence proves that the carboazidation process of brominated alkenes with 2-iodoesters proceeds in good yields. This demonstrates further the mildness and the high chemoselectivity of these radical reactions.



Scheme 15. Preparation of pyrrolizidinone and indolizidinone derivatives.

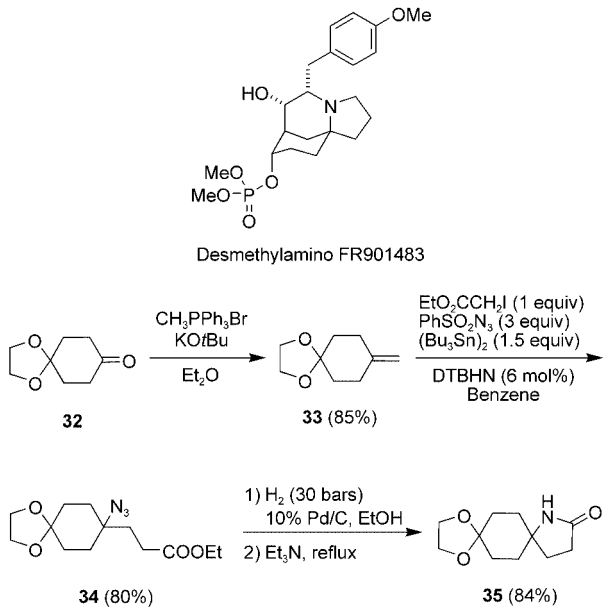
1-Azaspiro[4,4]nonan-2-ones and 1-azaspiro[4,5]decan-2-ones are important spirolactam building blocks for the synthesis of a wide range of alkaloids. Their synthesis is not trivial, since they contain an amino-substituted quaternary carbon center. Since the radical carboazidation reaction is particularly suitable for the preparation of such moieties, we developed a rapid two-step synthesis of spirolactams starting from methylenecycloalkanes.[33] The carboazidation of methylenecyclopentane and methylenecyclohexane affords azides **28** and **29** in 75% and 81% yield, respectively (Scheme 16).



Scheme 16. Rapid access to spirolactams.

These two reactions have been performed with one equivalent of the alkene and one equivalent of ethyl 2-iodoacetate. Hydrogenation of azides **28** and **29** (30 bar, 10% Pd/C) gives the amino esters that cyclize under heating in ethanol in the presence of triethylamine to afford the desired spirolactams **30** and **31**.

In order to show the utility of our approach for the synthesis of spirolactams, we decided to prepare compound **35**, an advanced intermediate in Wardrop's total synthesis of (±)-desmethylamino FR901483 (Scheme 17).[35] The synthesis started from commercially available monoprotected 1,4-cyclohexanedione **32**, which was first converted to the corresponding methylenecyclohexane **33**. Carboazidation of **33** afforded the azido ester **34** in 80% yield, which was readily converted by hydrogenation–lactamization to the desired spirolactam **35**.[33] This procedure for the preparation of **35** (3 steps, 57% overall yield) compares favorably with Wardrop's synthesis (5 steps, 53% overall yield).



Scheme 17. Preparation of spirolactam **35**, a building block for the synthesis of (±)-desmethylamino FR901483.

Conclusion

We are developing a novel radical process that allows us to introduce an azide moiety under very mild conditions. Sulfonyl azides have been used as azidating agents and nucleophilic radicals, such as secondary and tertiary alkyl radicals, are efficiently converted into azides. Interestingly, this process can be coupled with intramolecular and intermolecular C–C bond formation leading formally to a carboazidation process. Due to the versatility of the azido group, this reaction has an important synthetic potential as already demonstrated by the preparation of the core of several alkaloids, particularly those containing an aminated quaternary carbon center. Further extension of this chemistry towards the synthesis of other alkaloid skeletons is currently under investigation. Moreover, the design of new azidating agents allowing an easy purification of the products as well as to work under tin-free conditions is also underway.[36]

Acknowledgement

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[1] For general reviews on radical reactions, see: a) *Radicals in Organic Synthesis* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**; b) B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon, Oxford, **1988**; c) D. P. Curran in *Comprehensive Organic Synthesis, Vol. 4* (Eds.: B. M. Trost, I. Fleming, M. F. Semmelhack), Pergamon, Oxford, **1991**, p. 715 and 779; d) W. B. Motherwell, D. Crich, *Free Radical Chain Reactions in Organic Synthesis*, Academic Press, London, **1992**; e) J. Fossey, D. Lefort, J. Sorba, *Free Radicals in Organic Synthesis*, Wiley, Chichester, **1995**; f) C. Chatgilialoglu, P. Renaud in *General Aspects of the Chemistry of Radicals* (Ed.: Z. B. Alfassi), Wiley, Chichester, **1999**, p. 501.

[2] B. Giese, J. A. Gonzalez-Gomez, T. Witzel, *Angew. Chem.* **1984**, *96*, 51; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 69.

[3] D. P. Curran, M.-H. Chen, E. Spetzler, C. M. Seong, C.-T. Chang, *J. Am. Chem. Soc.* **1989**, *111*, 8872.

[4] For an exhaustive review, see: J. Byers in *Radicals in Organic Synthesis, Vol. 1* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, p. 72.

[5] For a leading reference, see: J. Boivin, A. C. Callier-Dublanchet, B. Quiclet-Sire, A. M. Schiano, S. Z. Zard, *Tetrahedron* **1995**, *51*, 6517.

[6] For an exhaustive review, see: L. Stella in *Radicals in Organic Synthesis, Vol. 2* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, p. 407.

[7] For an exhaustive review, see: C. Ollivier, P. Renaud in *Radicals in Organic Synthesis, Vol. 2* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, p. 93.

[8] For recent intramolecular cyclizations on imines, see: a) E. N. Prabhakaran, B. M. Nugent, A. L. Williams, K. E. Nailor, J. N. Johnston, *Org. Lett.* **2002**, *4*, 4197; b) R. Viswanathan, E. N. Prabhakaran, M. A. Plotkin, J. N. Johnston, *J. Am. Chem. Soc.* **2003**, *125*, 163.
[9] For general information about the chemistry of azides, see: *The Chemistry of The Azido Group* (Ed.: S. Patai), Wiley Interscience, New York, **1971**.
[10] For a pioneering work about the addition of radicals to azides, see: B. P. Roberts, J. N. Winter, *J. Chem. Soc. Perkin Trans. 2* **1979**, 1353.
[11] S. Kim, G. H. Joe, J. Y. Do, *J. Am. Chem. Soc.* **1994**, *116*, 5521.
[12] a) M. Kizil, B. Patro, O. Callaghan, J. A. Murphy, H. B. Hursthouse, D. Hibbs, *J. Org. Chem.* **1999**, *64*, 7856; b) B. Patro, J. A. Murphy, *Org. Lett.* **2000**, *2*, 3599.
[13] For a related application, see: M. Santagostino, J. Kilburn, *Tetrahedron Lett.* **1995**, *36*, 1365.
[14] D. S. Hays, G. C. Fu, *J. Org. Chem.* **1998**, *63*, 2796, and references therein.
[15] S. Kim, G. H. Joe, J. Y. Do, *J. Am. Chem. Soc.* **1993**, *115*, 3328.
[16] L. Benati, D. Nanni, C. Sangiorgi, P. Spagnolo, *J. Org. Chem.* **1999**, *64*, 7836.
[17] M. F. Sloan, W. B. Renfrow, D. S. Breslow, *Tetrahedron Lett.* **1964**, *5*, 2905.
[18] R. A. Abramovitch, W. D. Holcomb, *J. Chem. Soc. Chem. Commun.* **1969**, 1298.
[19] D. S. Breslow, M. F. Sloan, N. R. Newburg, W. B. Renfrow, *J. Am. Chem. Soc.* **1969**, *91*, 2273.
[20] H.-S. Dang, B. P. Roberts, *J. Chem. Soc. Perkin Trans. 1* **1996**, 1493.
[21] V. V. Zhdankin, A. P. Krasutsky, C. J. Kuehl, A. J. Simonsen, J. K. Woodward, B. Mismash, J. T. Bolz, *J. Am. Chem. Soc.* **1996**, *118*, 5192.
[22] F. L. Guyader, B. Quiclet-Sire, S. Seguin, S. Z. Zard, *J. Am. Chem. Soc.* **1997**, *119*, 7410.
[23] J. Xiang, P. L. Fuchs, *J. Am. Chem. Soc.* **1996**, *118*, 11986.
[24] S. Kim, J.-Y. Yoon, *J. Am. Chem. Soc.* **1997**, *119*, 5982.
[25] F. Bertrand, F. Le Guyader, L. Liguori, G. Ouvry, B. Quiclet-Sire, S. Seguin, S. Z. Zard, *C. R. Acad. Sci. Ser. IIc* **2001**, *4*, 547.
[26] C. Ollivier, P. Renaud, *J. Am. Chem. Soc.* **2000**, *122*, 6496.
[27] C. Ollivier, P. Renaud, *J. Am. Chem. Soc.* **2001**, *123*, 4717.
[28] S. Z. Zard, *Angew. Chem.* **1997**, *109*, 724; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 672.
[29] C. Ollivier, T. Bark, P. Renaud, *Synthesis* **2000**, 1598.
[30] E. D. Soli, P. DeShong, *J. Org. Chem.* **1999**, *64*, 9724, and references therein.
[31] D. S. Masterson, N. A. Porter, *Org. Lett.* **2002**, *4*, 4253.
[32] P. Renaud, C. Ollivier, P. Panchaud, *Angew. Chem.* **2002**, *114*, 3610; *Angew. Chem. Int. Ed.* **2002**, *41*, 3460.
[33] P. Panchaud, C. Ollivier, P. Renaud, S. Zigmantas, *J. Org. Chem.* **2004**, *69*, 2755.
[34] L. Chabaud, Y. Landais, P. Renaud, *Org. Lett.* **2002**, *4*, 4257.
[35] D. J. Wardrop, W. M. Zhang, *Org. Lett.* **2001**, *3*, 2353.
[36] P. Panchaud, P. Renaud, *J. Org. Chem.* **2004**, *69*, in press.

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