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Communications

An Unprecedented Radical Reaction of Benzotriazole Derivatives. A New Efficient Method for the Generation of Iminyl Radicals

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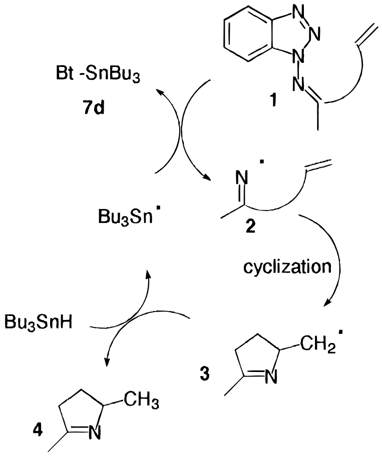
Iminyl radicals represent a new class of interesting intermediates in synthetic radical chemistry. Indeed, their cyclization on double bonds has been shown to yield Δ^1-pyrrolines, whereas opening of cyclobutylimino radicals offers a route to different substituted nitriles.[1] These species have been generated using various N-substituted imine derivatives incorporating a rather labile nitrogen−heteroatom bond under radical conditions. We report herein that *N*-benzotriazolylimines are suitable precursors for the generation of iminyl radicals and disclose a new radical chain process involving attack of a stannyl radical on a nitrogen atom.

At first sight indeed, *N*-benzotriazolylimines could have several attractive features: first, their preparation from the corresponding carbonyl derivatives and the readily available *N*-aminobenzotriazole[2] is an easy process, and moreover, these compounds should incorporate a relatively weak N−N bond. However, literature data in this field indicate that their use for the generation of iminyl radicals might be troublesome. Barton reported that the reaction of Bu_3SnH with an acyl derivative of *N*-hydroxybenzotriazole did not result in fragmentation to the corresponding acyloxy radical and then to an alkyl radical by decarboxylation.[3] To our knowledge, the only examples involving benzotriazole heterocycle in an apparently radical process are the oxydation of alcohols or ethers with *N*-chlorobenzotriazole[4] and the samarium diiodide reduction of α-(aminoalkyl)benzotriazole derivatives.[5]

Nevertheless, we have discovered that treatment of *N*-benzotriazolylimines **1** with Bu_3SnH in benzene containing a catalytic amount of AIBN leads to the formation of the corresponding iminyl radical **2** and *N*-(tributylstannyl)benzotriazole **7d**. Further evolution of **2** to a new radical **3**, either by cyclization or fragmentation, is followed by reduction of the latter to the expected product **4**, thus enabling propagation of the chain process (Scheme 1).

Scheme 1



Clearly, in this process, we have thus established a radical chain reaction involving in its propagation step an uncommon attack on a heterocyclic nitrogen tether by a stannyl radical. While halides, sulfides, and selenides have been widely used to generate radicals in the tin hydride method,[6] the literature offers few examples of nitrogen precursors in reactions of synthetic interest.[7] Diazirines have been used by Barton to achieve amination of carbon radicals in a nonchain process.[8]

The results obtained in the course of our study reflect the general pattern of reactivity for iminyl radicals.[1] Cyclization (for compounds **2a** and **3a**) and fragmentation reactions proceed in good to excellent yield (Table 1).

This new method for the generation of iminyl radicals has several attractive features. First, no slow addition of the tin hydride is required. The reaction generally starts after a short period of induction and is generally complete within 2 h. Even under these conditions, not a trace if any of the corresponding ketone that would have resulted from the premature reduction of the iminyl radical is detected in the crude reaction mixtures. Worthy of note is also the fact that in the case of compound **6a** derived from (−)-β-pinene an equimolar mixture of **6c** and **6d** resulting from the fragmentation, followed by a 1,5-hydrogen shift for the latter, is obtained in spite of our experimental conditions. Moreover, no difficulties were encountered in the separation of tin residues from the reaction mixture. *N*-(Tributylstannyl)benzotriazole (**7d**) undergoes a smooth protodestannylation on silica leading to benzotriazole as the only byproduct, the latter being easily separated by standard chromatography techniques and essentially quantitatively recovered.

Two mechanisms may be considered, depending on whether the tin radical attacks the N(1) or N(2) nitrogen atom (Scheme 2). Both imply the generation of a transient nitrogen-centered radical which upon subsequent rearomatization could liberate either a tin radical in a degenerate reaction or an iminyl radical **2** capable of further interesting synthetic evolution. The spectro-

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(1) See, for instance: (a) Boivin, J.; Fouquet, E.; Zard, S. Z. *Tetrahedron* **1994**, *50*, 1745. (b) Atmaran A.; Forrester A. E.; Gill, M.; Fhomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1721.

(2) Campbell, C. D.; Rees, C. W. *J. Chem. Soc. C* **1969**, 742.

(3) Barton, D. H. R.; Blundell, P.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1989**, *30*, 2341.

(4) (a) Rees, C. W.; Storr, R. C. *J. Chem. Soc. C* **1969**, 1474. (b) Pojer, P. M. *Aust. J. Chem.* **1979**, *32*, 2787.

(5) Aurrecoechea, J. M.; Fernandez-Acebes, A. *Tetrehedron Lett.* **1993**, *34*, 549.

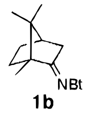
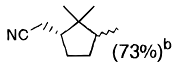
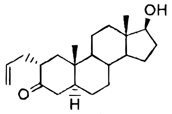
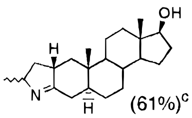
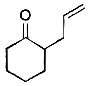
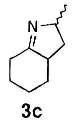
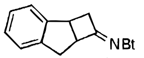
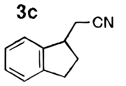
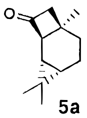
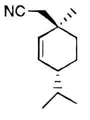
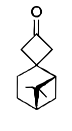
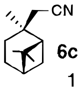
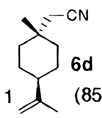
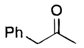
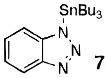
(6) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon−Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Curran, D. P. *Synthesis* **1988**, *417*, 489.

(7) Addition of stannyl radicals to aryl triazenes to form stannylamines and aromatic radicals by loss of nitrogen has been reported but has received no synthetic application in radical chemistry: Hollaender, J.; Neumann, W. P.; Alester G. *Chem. Ber.* **1972**, *105*, 1540. Radical addition to azide have been shown to proceed by a radical attack on nitrogen: Kim, S.; Joe G. H.; Do T. Y. *J. Am. Chem. Soc.* **1994**, 116, 5521.

(8) Barton, D. H. R.; Jaszberenyi, J. Cs.; Theodorakis, E. A. *J. Am. Chem. Soc.* **1992**, *114*, 5904.

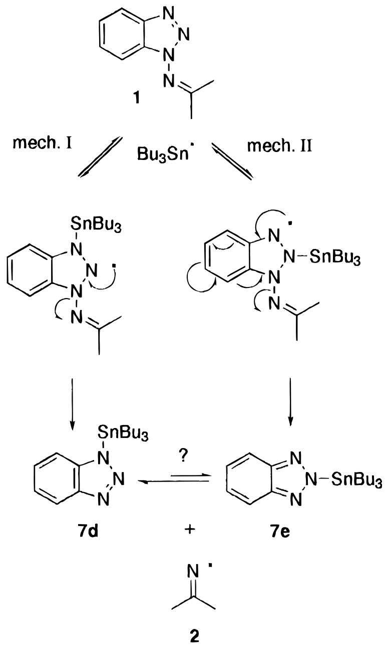
0022-3263/96/1961-1556$12.00/0

Table 1. Isolated Compounds after Iminyl Radical Generation

starting material [11] (yield from the ketone)	product (yield)
 **1b** (85%)[a]	 (73%)[b] **1c** d.r.= 3/2
 **2a**	 (61%)[c] **2c** d.r.= 3/1
 **3a**	 (73%)[c] d.r.= 3/2 **3c**
 **4b** (83%)[a]	 **4c** (86%)[b]
 **5a**	 **5c** (89%)[c]
 **6a**	 **6c** 1 / 1  **6d** (85%)[c]
 **7a**	 **7d** + PhMe + CH_3CN

[a] Obtained by condensation of *N*-aminobenzotriazole and ketone in toluene catalyzed by pTSA. [b] A 0.02 M solution of the *N*-benzotriazolylimine, Bu_3SnH, and AIBN (cat.) was refluxed for 2 h. [c] The above procedures were run consecutively without isolation of the intermediate *N*-benzotriazolylimine.

Scheme 2



scopic properties of the tin−benzotriazole adduct (see entry 7)[9] are consistent with the known compound **7d** and are in favor of a reaction through mecanism I; however, because of the known N(1)−N(3) stannotropy occuring on **7d**, mechanism II cannot be completely ruled out. Indeed, **7d** can be the product of a fast rearrangement of initially formed **7e**.

Since the benzotriazolyl moiety can be easily incorporated in various molecules using well-established benzotriazole chemistry,[10] further work is currently underway to generate other types of radicals using this methodology.

Acknowledgment. We thank Drs J. Boivin and S. Z. Zard for help and encouragement.

Supporting Information Available: Procedures and characterization data (3 pages).

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[9] Begtrup, M.; Elguero, J.; Faure, R.; Camps, P.; Estopa, C.; Ilavsky, D.; Fruchier, A.; Marzin, C.; De Mendoza, J. *Magn. Reson. Chem.* **1988**, *26*, 134.

[10] Katrytzky A. R.; S. Rachwall; G. J. Hitchings. *Tetrahedron* **1991**, 47, 2683−2732.

[11] The starting ketones were prepared according to: Lorette, N. B.; Howard, W. L. *J. Org. Chem.* **1961**, *26*, 3112 for **1b**. Tsuji, N.; Suzuki, J.; Shiota, M.; Takahashi, I.; Nishimura, S. *J. Org. Chem.* **1980**, *45*, 2729. Christiansen, R. G. U.S. Patent 3,287,355, 1966; *Chem. Abstr.* **1967**, *66*, 38145b for **2a**.; Ghosez, L.; Montaigne, R.; Roussel, A.; Vanlierde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615 for **4b**. Reference 1 for **5a** and **6a**.