Pergamon

Tetrahedron Letters 39 (1998) 5437–5438

TETRAHEDRON
LETTERS

On the use of 9-Borabicyclo[3.3.1]nonane as an Initiator for Low-Temperature Free-Radical Reductions

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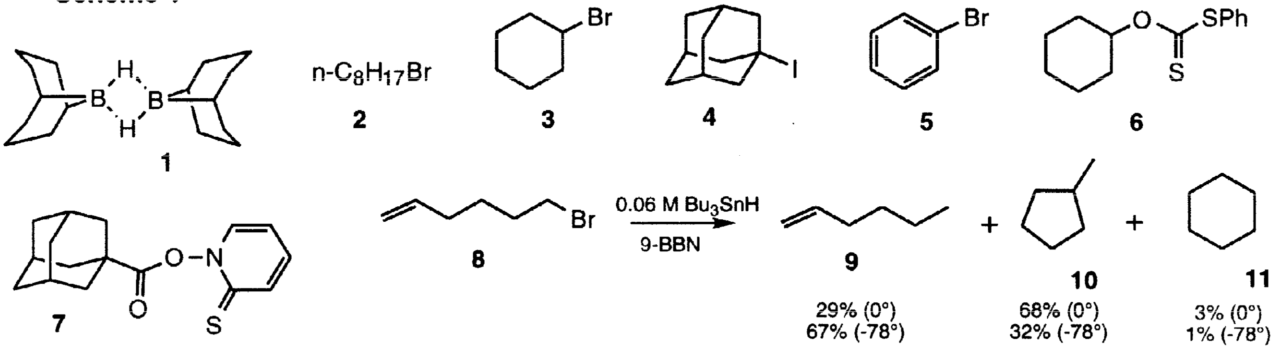
Received 27 March 1998; accepted 19 May 1998

Abstract: 9-Borabicyclo[3.3.1]nonane (9-BBN) (**1**) is an effective low-temperature initiator for use in stannane mediated free-radical reductions of a wide cross-section of typical radical precursors.

While there exist several classes of initiator for stannane-based free-radical reactions carried out at around room temperature and above, low temperature initiation has largely been restricted to photolysis or the use of triethylborane in the presence of oxygen.[1] Neither of these two techniques are appropriate for reactions involving compounds containing photo-labile or oxygen-sensitive functionalities; there are some suggestions however that reactions involving triethylborane can be initiated by very minor amounts of oxygen.[1]

Our recent interest in the development of new reagents for free-radical reactions at -78°C required that we locate a more user-friendly low-temperature initiator. Our requirements included the ability to initiate efficiently at -78° without the need for oxygen while maintaining acceptable yields in reasonable reaction times. We now report that 9-borabicyclo[3.3.1]nonane (9-BBN) (**1**)[2] efficiently initiates the reduction of a wide cross-section of typical radical precursors (**2** – **7**) by tributyl- and triphenyltin hydride, under nitrogen at both 0° and -78° in good to excellent yields.

Scheme 1



We began to explore the use of 9-BBN in radical chemistry through the low-temperature reaction of 1-bromooctane with tributyltin hydride. To that end, a toluene solution of tributyltin hydride (1 equiv.) was injected into a deoxygenated solution containing 1-bromooctane and (4 mol%)[3] 9-BBN in toluene at the required temperature and the resultant solution (ca. 0.06M in stannane) stirred under nitrogen for 2h at either 0° or -78°. At this time TLC analysis indicated the absence of starting material. Further analysis by GC revealed the formation of octane (by comparison with an authentic sample) in yields of 74% (0°) and 60% (-78°) through integration against an internal standard (decane). Importantly, when the reaction was repeated in the absence of 9-BBN, no reaction was observed after 2h. It is interesting to compare these results with those obtained using triethylborane as radical initiator; the use of 4 mol% Et_3B under nitrogen afforded octane

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PII: S0040-4039(98)01048-X

in 30% (-78°) and 19% (0°) yields after 2h. When these reactions were repeated under an aerobic atmosphere, as expected, improved yields (43% at -78°; 80% at 0°) were observed.

The generality of this procedure was explored by reacting tributyl- as well as triphenyltin hydride with a representative set of radical precursors (**2** – **8**);[4] Table 1 lists the results of these reactions.

Table 1. Yields of hydrocarbons (RH) obtained by reaction of radical precursors (RX) with tributyl- and triphenyltin hydride in toluene (ca. 0.06M) initiated by 9-BBN or Et_3B (4mol%) at 0° and -78°(in parentheses).

RX	**Bu_3SnH**			**Ph_3SnH**		
	9-BBN/N_2	Et_3B/O_2	Et_3B/N_2	9-BBN/N_2	Et_3B/O_2	Et_3B/N_2
2	74 (60)	80 (43)	19 (30)	73 (84)	83 (60)	25 (20)
3	70 (61)	76 (60)	14 (17)	100 (100)	90 (71)	22 (10)
4	84 (65)	78 (44)	20 (33)	83 (83)	61 (43)	22 (26)
5	72 (67)	75 (48)	15 (25)	100 (88)	87 (44)	11 (13)
6	78 (68)	46 (56)	0 (15)	86 (64)	74 (57)	0 (12)
7	96 (52)	75 (37)	14 (18)	88 (76)	79 (47)	19 (11)
8[a]	88 (70)	62 (47)	16 (0)	84 (80)	46 (67)	18 (0)

[a] Product consisted of a mixture of 1-hexene (**9**), methylcyclopentane (**10**) and cyclohexane (**11**).

Inspection of Table 1 reveals that at both temperatures, 9-BBN effectively initiates the reduction of a wide selection of common radical precursors by tributyl- and triphenyltin hydride in good to excellent yield. Importantly, these results are obtained under nitrogen, whereas similar initiation by Et_3B requires at least some oxygen present in the reaction.

In order to establish the intermediacy of radicals in these transformations, we examined the reaction of 6-bromo-1-hexene with Bu_3SnH/9-BBN under similar conditions. GC analysis indicated the formation 1-hexene (**9**), methylcyclopentane (**10**) and cyclohexane (**11**) in the relative yields given in Scheme 1 and in the overall yield listed in Table 1. Application of the appropriate integrated rate equation[5] leads to values of k_c/k_H of 0.04 (0°) and 0.006 (-78°), in excellent agreement with the expected values of 0.05 and 0.006 based on the well established kinetic equation for the cyclization of the 5-hexenyl radical.[6] These data leave little doubt that the low-temperature reductions initiated by 9-BBN presented in this report are radical in nature.

We thank the Australian Research Council for financial support.

Notes and References

1. Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K., *Bull. Chem. Soc. Jpn.*, **1989**, *62*, 143. Curran, D. P.; Nanni, *Tetrahedron: Asymmetry*, **1996**, *7*, 2417.
2. 9-BBN is an air-stable dimeric solid useful for selective hydroborations. For examples, see: Knights, E. F.; Brown, H. C., *J. Am. Chem. Soc.*, **1968**, *90*, 5280. Knights, E. F.; Brown, H. C., *J. Am. Chem. Soc.*, **1968**, *90*, 5281. Brown, H. C.; Krishnamurthy, S.; Yoon, N. M., *J. Org. Chem.*, **1976**, *41*, 1778.
3. Based on monomeric 9-BBN.
4. Giese, B., *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, **1986**, Pergamon Press, Oxford. Regitz, M.; Giese, B., *Radicale, Houben-Weyl Methoden der Organischen Chemie*, **1989**, Vol E 19a, Georg Thieme, Stuttgart. Perkins, M. J., *Radical Chemistry*, **1994**, Ellis-Horwood, New York.
5. Rate equation: $d[\mathbf{9}]/d[\mathbf{10}] = k_c/(k_H[Bu_3SnH])$ where k_c and k_H are the rate constants for the formation of **9** and **10** respectively.
6. Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickrema, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U., *J. Am. Chem. Soc.*, **1985**, *107*, 4594. Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C., *J. Am. Chem. Soc.*, **1981**, *103*, 7739. Dakternieks, D.; Henry, D. J.; Schiesser, C. H., *J. Org. Chem.*, submitted for publication.