A Remarkably Efficient Initiation by 9-BBN in the Radical Addition Reactions of Alkanethiols to Alk-1-enes

Yuzuru Masuda, Masayuki Hoshi, Yutaka Nunokawa and Akira Arase*
Kitami Institute of Technology, Department of Industrial Chemistry, Koencho Kitami 090, Japan

A catalytic amount of 9-borabicyclo[3.3.1]nonane (9-BBN) initiates radical addition reactions of alkanethiols to alkenes under very mild conditions to provide the corresponding dialkyl sulphides almost quantitatively.

Organoboranes can participate in either ionic or radical reactions.[1] However, relatively few studies have been reported on the application of organoboranes as initiators for radical reactions.[2,3] The radical addition reactions of alkanethiols to alkenes have been extensively investigated and most of the reactions were initiated by thermal decomposition of peroxides or azo compounds, by UV irradiation, or by radiolysis.[4]

In the course of our study on sulphur-containing organoboranes we found that the presence of a catalytic amount of 9-borabicyclo[3.3.1]nonane (9-BBN) and its derivatives, *B*-hexyl-9-BBN and *B*-methoxy-9-BBN, markedly initiated the radical addition reaction of alkanethiols to alkenes.

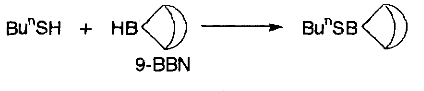
Without any additives, the reactions of alkanethiols with alkenes were very sluggish under the reaction conditions used in the present study. For example, the reaction of 5 mmol of butanethiol in 10 ml of tetrahydrofuran (THF) with 5 mmol of hex-1-ene provided the addition product, butyl hexyl sulphide, in only 0.2% yield after 24 h at room temperature.

In the presence of 9-BBN, the reaction was efficiently promoted. Thus, the addition of 0.5% of 9-BBN (0.025 mmol) to the above solution achieved nearly quantitative yield of butyl hexyl sulphide within 1 h at 0 °C. In this case the reaction proceeded well even in the dark. However, the reaction was completely inhibited by the presence of galvinoxyl, a radical trapping agent. These facts indicated that 9- BBN participated in the initiation of the radical addition reaction of butanethiol to hex-1-ene see eqn. (1) and Table 1.

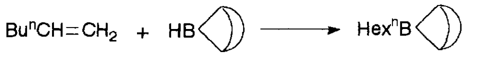
Under the above reaction conditions, the reaction of butanethiol with 9-BBN is very sluggish [eqn. (2)], while the reaction of hex-1-ene with 9-BBN proceeds easily to provide *B*-hexyl-9-BBN [eqn. (3)].[5] Accordingly, there was a possibility of the formation of *B*-hexyl-9-BBN before or during the addition reaction of butanethiol to hex-1-ene and, thus, an ambiguity as to which of the species 9-BBN or *B*-hexyl-9-BBN acted as the initiator.

$$\mathrm{Bu^nSH} + \mathrm{H_2C{=}CHBu^n} \xrightarrow{\mathrm{THF}} \mathrm{Bu^nS\,Hex^n} \qquad (1)$$

To clarify this ambiguity, two addition reactions of butanethiol to 2-methylbut-2-ene were examined, thus, one in the presence of 0.5% of 9-BBN and the other in the presence of 0.5% of *B*-hexyl-9-BBN prepared just before the use.[5] Both reactions were carried out at 0 °C because at this temperature the hydroboration of 2-methylbut-2-ene with 9-BBN was very slow and, therefore, the formation of *B*-(1,2-dimethylpropyl)-9-BBN should be negligible [eqn. (4)].[6] After 6 h the former provided butyl 1,2-dimethylpropyl sulphide in 92% yield and



(2)



(3)

Table 1 Yields of butyl hexyl sulphide from the addition reaction of butanethiol and hex-1-ene with different additives

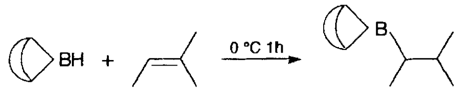
Additive	Reaction time/h[a]	Yield (%)
None	24	0.2
9-BBN (0.5%)	1	>99
	1[b]	>99
Galvinoxyl (1%)	1	0
B-Hexyl-9-BBN (1%)	1	98

[a] Reactions at room temp. unless otherwise indicated. [b] Reaction at 0 °C.

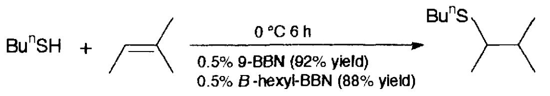
Table 2 Reactions[a] of alkanethiols with terminal alkenes in the presence of 9-BBN

R^1 of $R^1CH{=}CH_2$[a]	R^2 of R^2SH[a]	Reaction time/h	Yield[b] of $R^1CH_2CH_2SR^2$ (%)
Bu^n	Bu^n	1	>99
	Bu^s	3	96
	Bu^t	3	91
	$c\text{-}C_6H_{11}$	3	92
	CH_2Ph	3	90
$c\text{-}C_6H_{10}$	Bu^n	1	99[c]
	Bu^s	3	97[c]
	Bu^t	3	80[c]
$Me_3SiCH_2Si\text{–}CH_2$	Bu^n	1	99
	Bu^s	3	80
	Bu^t	3	78

[a] To 10 ml of THF, 5 mmol of alkene, 0.025 mol of 9-BBN (0.5%) in THF and 5 mmol of alkanethiol were added successively at 0 °C and the mixture was stirred at the same temperature. [b] Determined by GLC. [c] The product is $c\text{-}C_6H_{11}CH_2SR^2$.



(4)



(5)

the latter provided the same compound in 88% yield indicating that both 9-BBN and *B*-hexyl-9-BBN could initiate the addition reaction effectively [eqn. (5)]. It is interesting that 9-BBN, having a boron–hydrogen bond, can initiate the radical addition reaction, because, to our knowledge, there have been no reports where such types of organoborane were utilized as the initiator of radical reactions.

On the other hand, *B*-hexyl-9-BBN also initiated the reaction of butanethiol with hex-1-ene very effectively providing 98% yield of the addition product after reaction at room temperature for 1 h [eqn. (1)].

In addition, the high yield obtained in the presence of *B*-hexyl-9-BBN, having a trialkylborane structure, is an interesting result because it suggests that a wide variety of trialkylboranes could be used as the initiator. However, triethylborane and trihexylborane were far less effective than 9-BBN as the initiator. Thus, in the presence of 1% of triethylborane the reaction of butanethiol with hex-1-ene provided butyl hexyl sulphide in 58% yield after reaction at room temperature for 1 h and in 29% yield at 0 °C for 1 h. The presence of trihexylborane also showed a similar initiating effect to triethylborane (43% yield after 1 h at room temp. and 31% after 1 h at 0 °C).

Although slightly inferior to 9-BBN, *B*-methoxy-9-BBN also showed a similar effect providing 77% yield of butyl hexyl sulphide under the same reaction conditions (room temp. for 1 h).

The initiation by 9-BBN was effective not only in the addition reactions of primary alkanethiols to terminal alkenes but also in the addition reactions of *sec*- or *tert*-alkanethiols to terminal alkenes giving high yields of the corresponding dialkyl sulphides (Table 2).

The dialkyl sulphides thus obtained were isolated directly from the reaction mixture by simple distillation without any work-up procedure. Accordingly, the present finding, the highly efficient initiation of radical reactions by 9-BBN, seems to be of interest not only in both radical and borane chemistry but also provides a practical method for the preparation of dialkylsulphides.

Received, 25th June 1991; Com. 1/03177E

References

1 See, for example, A. Pelter, K. Smith and H. C. Brown, *Borane Reagents*, Academic Press, London, 1988.
2 A. Arase, M. Hoshi and Y. Masuda, *Chem. Lett.*, 1979, 961; M. Hoshi, Y. Masuda and A. Arase, *Chem. Lett.*, 1984, 195.
3 K. Oshima and K. Utimoto, *J. Synth. Org. Chem., Jpn.*, 1989, **47**, 40.
4 See, for example, P. I. Abell, in *Free Radicals*, ed. J. K. Kochi, Wiley, New York, 1973, vol. II, p. 63.
5 H. C. Brown, R. Liotta and C. C. Scouten, *J. Am. Chem. Soc.*, 1974, **96**, 7765.
6 H. C. Brown, R. Liotta and C. S. Scouten, *J. Am. Chem. Soc.*, 1976, **98**, 1976.