

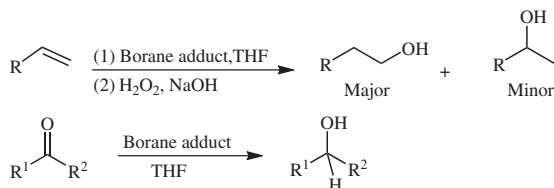
New polymeric sulfide-borane complexes: convenient hydroborating and reducing reagents

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New polymeric borane adducts have been synthesized from polymeric sulfides, which are solids with a minimal odor. Adducts containing a high concentration of borane have significant stability and are soluble in tetrahydrofuran. They act as hydroborating and reducing reagents with behavior similar to that of borane-methyl sulfide, making them attractive borane sources.



Keywords: polymeric sulfides; borane adducts; hydroboration; reduction; carbonyl compounds

1. Introduction

Borane complexes are highly versatile reagents with numerous applications in organic syntheses and industrial processes (1–3). The most commonly used are borane-tetrahydrofuran ($\text{BH}_3 \cdot \text{THF}$) (4) and borane-dimethyl sulfide ($\text{BH}_3 \cdot \text{SMe}_2$, BMS) (5). However, both these reagents possess certain unfavorable characteristics (5). $\text{BH}_3 \cdot \text{THF}$ is commercially available only as a dilute solution, nominally 1.0 M in BH_3 , and it undergoes slow decomposition via cleavage of THF at room temperature. BMS is free from these disadvantages, as it is a neat complex, 10.0 M in BH_3 , can be used in a variety of solvents and is highly stable. However, BMS liberates a stoichiometric amount of water-insoluble dimethyl sulfide, which has an obnoxious odor, high volatility and flammability, thereby creating environmental and safety problems, particularly for large scale use. This prompted Brown and co-workers (6) in 1992 to introduce 1,4-oxathiane

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as a less volatile carrier for borane. Subsequently, Brown and co-workers (7, 8) demonstrated the utility of a series of liquid organic sulfides as borane carriers, bis(hydroxymethyl)sulfide (9) possessing the additional advantage of being water soluble, while 2-(perfluorooctyl)ethyl methyl sulfide (10) is a recyclable borane carrier. A few solid borane complexes with bis-sulfides (2a) have also been patented, and borane complexes with hindered tertiary amines such as *N*-ethyl-*N*-iso-propylaniline (11) or 5-ethyl-2-methylpyridine (12) have been advocated. Clearly, there is a strong desire for safe borane carriers that can be easily handled. However, to be attractive as replacements for the commonly used complexes, alternative adducts must be fairly high in borane content (to avoid having to transport large quantities), be stable enough for long-term storage, have distinct advantages in terms of handling (*e.g.* avoiding obnoxious odors, avoiding high flammability or allowing easy recovery of the carrier), be relatively inexpensive and match $\text{BH}_3 \cdot \text{THF}$ or BMS in terms of reactivity profile. To date, no other complex has fulfilled these criteria sufficiently well to rival the common complexes.

Polymer-bound borane complexes offer the possibility of stable and easily handled materials of low volatility, with minimal odor and with easily recoverable polymeric carriers. Indeed, a number of polymer-bound complexes have been reported, including BH_3 complexes of several cross-linked polymeric sulfides (13), a cross-linked poly(4-vinylpyridine)-borane complex in which the borane content was up to 7.8 mmol/g (14), and borane and haloborane complexes of poly(propylene sulfide) grafted onto cross-linked polystyrene (15). Although all of these reagents have been used for hydroboration of alkenes and/or reduction of aldehydes and ketones to produce the corresponding alcohols, acid catalysis was required in the case of the poly(vinylpyridine) complex (16). Thus, its reactivity profile is significantly different (and less useful) from that of borane-THF or BMS, so it cannot be viewed as a potential replacement. A similar situation pertains to polymer-supported ethylenediamine borane complexes prepared using a Merrifield resin or a 1,6-hexanediol diacrylate-cross-linked polystyrene resin (17). These materials have been used for reduction of aldehydes to the corresponding alcohols in high yields at room temperature, but the concentration of borane in the complexes is already low and the use of a two molar excess of the polymeric reagent was required (17). However, the polymer could be regenerated easily and reused without loss in reactivity.

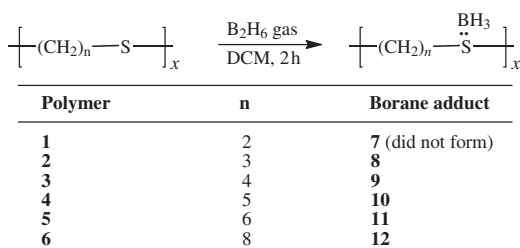
The borane content of the grafted poly(propylene sulfide) complex was also low (around 2.44 mmol BH_3/g) (15). A higher borane content (up to 7.05 mmol BH_3/g of polymer) was claimed for a homo poly(propylene sulfide) complex, but this material was prepared and used only as a dilute solution in dichloromethane and it is not clear whether removal of the solvent would have left a solid with such a high concentration of borane (15). There are no reports of these complexes ever having been applied to synthesis, possibly because of the low borane content of the solid borane-polymer complex and the inconvenience of transporting a dilute solution of the homo poly(propylene sulfide)-borane complex.

Our long-standing interests in the use of solids in green methodologies (18) and in boron chemistry (1, 19) led us to consider the possibility of other polymeric sulfides as suitable borane carriers. In particular, we wished to develop complexes possessing high molarity in BH_3 , based on solids that are easy to prepare, convenient to handle, have mild odor and low volatility and are environmentally benign. We now report the results of our efforts to develop such reagents.

2. Results and discussion

Polymeric sulfides 1–6 were synthesized based on literature procedures (for the synthesis of polymeric materials, see (20)). Unlike poly(propylene sulfide), these contain unbranched alkylene chains. The complexing ability of the polymers toward borane was investigated by bringing them

into contact with $\text{BH}_3 \cdot \text{THF}$ or diborane gas using four procedures: (i) reaction of neat solid sulfide **1–6** with $\text{BH}_3 \cdot \text{THF}$, (ii) reaction of neat polymer with diborane gas, (iii) reaction of a solution of the polymeric material with $\text{BH}_3 \cdot \text{THF}$ and (iv) reaction of a solution of the polymeric material with diborane gas. Interestingly, and uniquely, no uptake of borane to give complex **7** was observed for the sulfide **1** ($n = 2$) under any of the conditions tried. This was surprising in view of the reported uptake of up to 7 mmol/g of borane by poly(propylene sulfide), which is simply a methyl-substituted version of this polymer. The other linear polymeric sulfides (**2–6**) all absorbed significant quantities of borane by all of the procedures, and, after considerable experimentation, it was found that the passage of diborane gas, generated from $\text{BF}_3 \cdot \text{OEt}_2$ and sodium borohydride (*2I*), into a solution of the polymeric sulfide (3 g) in dichloromethane (20 ml) at room temperature was the most convenient method for producing the corresponding borane adducts **8–12** (Scheme 1). In this procedure, the adducts were precipitated, but were not separated by filtration or decantation. Instead, the solvent was removed by blowing nitrogen over the mixture to leave the solid adducts. Table 1 gives their borane content and ^{11}B NMR data. We also placed a sample of adduct **8** under oil pump vacuum for 20 min, during which there was no loss of mass, indicating that on a larger scale, the solvent could be removed under reduced pressure rather than by blowing with nitrogen.



Scheme 1. Synthesis of the polymeric sulfide-borane adducts **8–12**.

The effect of other solvents in the preparative procedure was also tested. Adducts resulting from reaction in chloroform or diglyme possessed a hydride content that was lower by about 10% than for complexes formed in dichloromethane. Use of more dilute dichloromethane solutions also resulted in lower hydride content of the precipitated complexes. The gas analyses of adducts **8–12** indicated that around two-thirds of the total sulfur atoms had been coordinated with borane. The ^{11}B NMR spectra of all complexes showed a single resonance at $\delta -20.8$ to -20.9 ppm, consistent with the formation of adducts.

Table 1. Preparation of borane adducts **8–12** from the corresponding polymeric sulfides **2–6** according to Scheme 1.^a

Polymeric sulfide	Adduct ^b	n	B/S ratio ^c	mmol BH_3/g
2	8	3	0.68	8.17
3	9	4	0.65	6.69
4	10	5	0.65	5.85
5	11	6	0.67	5.36
6	12	8	0.68	4.44

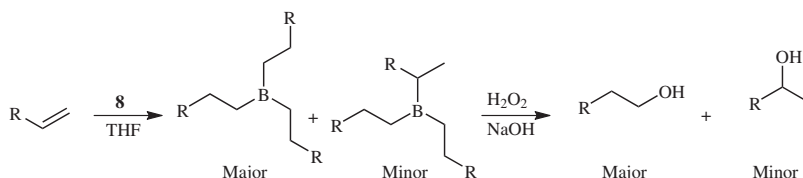
Notes: ^aAll adducts were prepared by passing diborane gas into a suspension of the polymeric sulfides (3 g) in dichloromethane (20 ml).

^bWhite powders at room temperature.

^cRatio of BH_3 molecules (estimated by measurement of hydrogen evolved on hydrolysis in $\text{THF}:\text{glycerol}:\text{3 M HCl}$ (1:1:1) to S atoms present (measured by microanalysis).

The borane adducts **8–12** were white powders at room temperature and exhibited a very mild ‘borane’ odor when transferred in air. They were soluble in THF, which is typically used for hydroboration and reduction reactions. They appeared to be stable over long periods under nitrogen (there was no change in borane content after three weeks at room temperature under nitrogen and the hydride content had reduced by only 30% even after five years in a simple septum-sealed flask). They were fairly stable even in air, decomposing only slowly on standing in air at room temperature. The stability of the complexes in air was readily ascertained by recording infrared spectra at regular intervals (from 5 min to 24 h). Two distinct peaks at 2398 and 1095 cm^{-1} , which may be attributed to B–H and B–S stretching vibrations, respectively (22), appeared in the spectra of freshly prepared pure samples of the complexes. No peak around 3200 cm^{-1} corresponding to boric acid was observed initially. After samples had stood for 4 h in air, the peaks at 2398 and 1095 cm^{-1} began to diminish noticeably and a strong peak around 3200 cm^{-1} began to appear, thereby indicating hydrolysis of the adduct. Only on prolonged standing did the solid begin to darken. This significant stability in air enabled the solid borane adducts to be weighed on a simple balance without protection from air. Their very mild odors were further indication that they did not release borane readily, and thermogravimetric analysis of adduct **8** indicated that no loss of borane occurred until above 110°C. These features and their reasonable solubilities make the adducts potentially attractive and easy-to-handle reagents.

To establish the synthetic applicability of the new borane complexes, hydroboration–oxidation of alkenes was studied. Initially, hydroboration–oxidation of 1-octene (Scheme 2; $\text{R} = n\text{-C}_6\text{H}_{13}$) in THF at room temperature was conducted with the borane adducts **8–12** for 4 h. In each case, a high yield (by GC) of a mixture of 1- and 2-octanol was obtained, indicating that the reactivities of the new borane adducts were comparable with those of BMS (**4**) and $\text{BH}_3 \cdot \text{THF}$ (23). Thus, hydroboration of other representative alkenes was conducted initially with **8** as the borane adduct (Scheme 2). Adduct **8** was chosen because its polymer’s repeating unit has the lowest relative mass, so that its borane content is higher in terms of mass than the others. The results are recorded in Table 2.



Scheme 2. Hydroboration–oxidation of alkenes with the borane adduct **8**.

Table 2. Hydroboration–oxidation of alkenes with the borane adduct **8** in THF according to Scheme 2 at room temperature for 4 h.^a

Alkene	Product	Yield (%) ^b
1-Octene	1-Octanol	59
	2-Octanol	2
1-Hexene	1-Hexanol	71
	2-Hexanol	2
Cyclopentene	Cyclopentanol	80
Cyclohexene	Cyclohexenol	86

Notes: ^aAlkene (9.0 mmol) was added to a solution of **8** (ca. 3.6 mmol BH_3) in THF (14 ml) at 0–5°C and stirred for 4 h at room temperature. The mixture was oxidized at 0–5°C using NaOH (3.0 M, 3.0 ml) and H_2O_2 (30%, 3.5 ml) followed by warming to room temperature for 1 h to ensure complete oxidation.

^bBy GC analysis using hexadecane as internal standard.

The procedure involved the addition of an alkene (9.0 mmol) to the solution of borane complex (3.6 mmol of BH_3) in THF at $0-5^\circ\text{C}$ followed by stirring for 4 h at room temperature and then oxidative work up with alkaline hydrogen peroxide. The alcohols produced were analyzed by quantitative GC. The yields of alcohols obtained were in the range of 61–86%.

Several experiments were conducted in order to find conditions under which higher yields of alcohols could be obtained. It was found that the use of a longer reaction time (16 h) gave satisfactory results. Therefore, this procedure was applied to a range of alkenes. The results obtained are recorded in Table 3.

Reactions conducted over this longer reaction period gave good yields (84–99%). The regioselectivities of hydroboration of 1-hexene and styrene were similar to those reported for BMS (5) and $\text{BH}_3 \cdot \text{THF}$ (24). Thus, the hydroboration of 1-hexene formed 1- and 2-hexanols in the ratio of 84:4, while styrene gave 1- and 2-phenylethanols in the ratio 79:12. The hydroboration of 1-methylcyclohexene produced *trans*-2-methylcyclohexanol in essentially quantitative yield. The adduct **8** therefore functioned very similarly to BMS in hydroboration reactions, but with the significant advantage that the reactions are odor-free and do not liberate dimethyl sulfide.

To establish further the synthetic potential of the new borane adduct **8**, the reduction of representative organic functional groups was studied (*e.g.* see Scheme 3 for the reduction of aldehydes and ketones) and the results are recorded in Table 4.

The procedure adopted was to add a standard solution of the organic compound in THF to an appropriate quantity of complex in THF at 0°C and then reflux the mixture for 4 h. The excess borane was then quenched with methanol and the product was analyzed by GC. Reduction of most substrates was straightforward and gave high yields (85–100%) of the corresponding alcohols, similar to BMS (24, 25). Although the reactions were carried out under standard conditions of reflux for 4 h, such forcing conditions were often not necessary. However, the reduction of benzamide was slow and a yield of only 66% of benzylamine was obtained even after a longer reaction time (16 h).

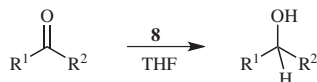
The sulfide polymer could be recovered following either hydroboration or reduction reactions. The polymeric material **2** was precipitated as a white solid by the addition of diethyl ether during the work-up process and was removed by filtration. It was washed with a saturated solution of sodium hydroxide to remove any boric acid, then washed thoroughly with water and left to dry in a vacuum oven. The recovered polymer was reused again to prepare **8**. The adduct obtained was virtually identical to the initial one. It had the same borane content and showed the same behavior when used as a hydroborating and reducing agent.

Table 3. Hydroboration–oxidation of alkenes with the borane adduct **8** in THF according to Scheme 2 at room temperature for 16 h.^a

Alkene	Product	Yield (%) ^b
1-Octene	1-Octanol	81
	2-Octanol	4
1-Hexene	1-Hexanol	80
	2-Hexanol	4
Styrene	2-Phenylethanol	79
	1-Phenylethanol	12
1-Methylcyclohexene	<i>trans</i> -2-methylcyclohexanol	99
Cyclopentene	Cyclopentanol	84
Cyclohexene	Cyclohexanol	86

Notes: ^aAlkene (9.0 mmol) was added to a solution of **8** (*ca.* 3.6 mmol of borane) in THF (14 ml) at $0-5^\circ\text{C}$ and stirred for 30 min at 0°C and 16 h at room temperature. The mixture was oxidized at $0-5^\circ\text{C}$ using NaOH (3.0 M, 3.0 ml) and H_2O_2 (30%, 3.5 ml) followed by warming to room temperature for 1 h to ensure complete oxidation.

^bBy GC analysis using hexadecane as internal standard.

Scheme 3. Reduction of aldehydes and ketones with the borane adduct **8**.Table 4. Reduction of functional groups with **8** in THF under reflux for 4 h.^a

Starting material	8 (mol. eq.)	Product	Yield (%) ^b
Benzaldehyde	0.4	Benzyl alcohol	100
2-Hexanone	0.4	2-Hexanol	94
Caproic acid	1.2	1-Hexanol	92
Benzoic acid	1.2	Benzyl alcohol	90
Methyl benzoate	0.8	Benzyl alcohol	99
Butyl benzoate	0.8	Benzyl alcohol	97
Phenyl benzoate	0.7	Benzyl alcohol	88
Benzamide ^c	1.9	Benzylamine	51 (66) ^d
Cyclohexene oxide	0.4	Cyclohexanol	85

Notes: ^aOrganic compound (5 mmol) was added to a solution of **8** in THF and the mixture was stirred at 0°C for 30 min and then refluxed for 4 h. Methanol (3 ml) was added and the mixture was stirred for 15 min, then the product was extracted into diethyl ether (20 ml).

^bBy GC analysis using hexadecane as internal standard.

^cAfter reaction HCl (1.0 M, 3 ml) was added and the mixture was refluxed, cooled to 0°C, then diethyl ether (20 ml) and NaOH (pellets) were added to neutralize the solution followed by the separation of the organic layer.

^dThe reaction time was 16 h.

Our attention was next turned to the use of borane adduct **11**, to test whether it showed any significant differences in activity compared with **8**. Adduct **11** was tested in hydroboration of representative alkenes and reduction of representative carbonyl compounds under conditions similar to those used with adduct **8** (Schemes 2 and 3, respectively). The results obtained are recorded in Tables 5 and 6, respectively.

The results recorded in Table 5 clearly indicated that adduct **11** can be used as a hydroborating agent. The small variations in yields obtained compared with those obtained from similar reactions involving the use of adduct **8** may be due to losses during work-up. However, the selectivities observed were entirely comparable. For example, hydroboration of 1-octene produced a mixture of 1- and 2-octanols in 77% and 4% yields, respectively, compared with 81% and 4%, respectively, with adduct **8**. With styrene, 1- and 2-phenylethanols were formed in the ratio of 84:13, similar to the 79:12 ratio obtained with adduct **8**.

Table 5. Hydroboration–oxidation of alkenes with the borane adduct **11** in THF at room temperature for 16 h.^a

Alkene	Product	Yield (%) ^b
1-Octene	1-Octanol	77
	2-Octanol	4
1-Hexene	1-Hexanol	73
	2-Hexanol	5
Styrene	2-Phenylethanol	84
	1-Phenylethanol	13
1-Methylcyclohexene	<i>Trans</i> -2-methylcyclohexanol	83
Cyclopentene	Cyclopentanol	88

Notes: ^aAlkene (9.0 mmol) was added to a solution of **11** (ca. 3.6 mmol BH₃) in THF (15 ml) at 0–5°C and was stirred for 30 min at 0°C and for 16 h at room temperature. The reaction mixture was oxidized at 0–5°C using NaOH (3.0 M, 3.0 ml) and H₂O₂ (30%, 3.5 ml) followed by warming to room temperature for 1 h to ensure complete oxidation.

^bBy GC analysis with hexadecane as an internal standard.

Table 6. Reduction of some carbonyl compounds with borane adduct **11** in THF.^a

Entry	Starting material	11 (mol. eq.)	Product	Yield (%) ^b
1	Benzaldehyde	0.4	Benzyl alcohol	100
2	2-Hexanone	0.4	2-Hexanol	84
3	Caproic acid	1.1	1-Hexanol	93
4	Ethyl benzoate	0.8	Benzyl alcohol	94

Notes: ^aCarbonyl compound (5.0 mmol) was added to a solution of **11** in THF and stirred at 0°C for 30 min and refluxed for 4 h. Methanol (3 ml) was added and the mixture was stirred for 15 min then extracted with diethyl ether (20 ml).

^bBy GC analysis using hexadecane as internal standard.

Table 6 shows that adduct **11** can also be used as a reducing reagent for various carbonyl compounds to produce the corresponding alcohols in high yields (84–100%). Again, the reactions were carried out under standard conditions at reflux for 4 h, although not all examples needed such forcing conditions.

3. Conclusions

In conclusion, borane adducts derived from polymeric sulfides are solids of high hydride content that can be readily weighed in air. Their mild smell, good solubility in THF and reactivity comparable to that of BMS, make them attractive borane sources. Consequently, complex **8**, in particular, is a highly promising, new hydroborating reagent, which might well be suitable for large-scale industrial application.

4. Experimental section

4.1. General

All reactions were performed under a nitrogen atmosphere. Glassware was oven-dried, assembled hot and allowed to cool under a stream of nitrogen gas. All reagents were purchased from commercial sources and used as received. THF was distilled from sodium benzophenone ketyl and other solvents were purified by standard procedures (26). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. ¹H and ¹¹B NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400 MHz for ¹H or 128 MHz for ¹¹B measurements. Chemical shifts δ are reported in parts per million (ppm) relative to TMS and BF₃ · Et₂O, respectively. GC analyses were carried out on a Shimadzu Gas Chromatograph fitted with a ZEBRON ZB-5 (5% phenyl polysiloxane) 30 m length column. The GC conditions used for analysis were: 40°C for 1 min, ramped to 250°C at 20°C/min and held for 3 min. The injection temperature was 250°C and the detection temperature was 250°C. Hexadecane was used as a GC standard. Microanalyses were performed by Warwick analytical service at the University of Warwick.

4.2. Borane adducts: typical experimental procedure for preparation of borane adduct **8**

Diborane gas generated by the reaction of sodium borohydride (5.67 g, 0.15 mol) in diglyme (50 ml) with BF₃ · Et₂O (24.5 ml, 0.20 mol) was passed slowly through a dichloromethane (25 ml) solution of polymeric sulfide **2** (3.0 g) at room temperature over a period of 2 h. Excess diborane was allowed to absorb in THF (15 ml) in a second bubbler. A white solid precipitated out in the

flask containing the polymer when passage of the borane gas was nearing completion. The solvent was removed from the mixture by blowing with nitrogen. The resulting borane-sulfide adduct **8** was analyzed for active hydride by a standard procedure (27) using THF:glycerol:3 M HCl (1:1:1) as the hydrolyzing mixture. The ratio of BH₃ units to S atoms in the polymer was *ca.* 0.68. δ_B (128 MHz, CDCl₃; Me₄Si) –20.9.

4.3. Hydroboration–oxidation of alkenes: typical procedure for hydroboration of 1-hexene with **8**

Adduct **8** (0.44 g, 3.6 mmol BH₃) was placed in an oven-dried 50 ml flask protected by a rubber septum. The flask was cooled to 0°C under a stream of nitrogen and freshly distilled THF (14 ml) was added. 1-Hexene (0.757 g, 9.0 mmol) was added and the mixture was stirred at 0°C for 30 min and then at room temperature for 16 h. The reaction mixture was cooled to 0°C and NaOH (3.0 M, 3.0 ml) was added, followed by slow addition of hydrogen peroxide (30%, 3.5 ml). The contents were further stirred at room temperature for 1 h to ensure complete oxidation. Hexadecane (0.75 g) was added followed by the addition of diethyl ether (10 ml) to precipitate the liberated polymeric sulfide. GC of the organic layer showed that the combined yield of 1- and 2-hexanols was 84% in *ca.* 80:4 ratio.

4.4. Reduction of functional groups: typical procedure for reduction of benzaldehyde with **8**

A 50 ml two-neck flask equipped with a reflux condenser and a magnetic bar was flushed with nitrogen and charged with **8** (0.24 g, 2.0 mmol BH₃) and cooled to 0°C. THF (10 ml) was added and the resulting colorless solution was cooled to 0°C. Benzaldehyde (0.53 g; 5.0 mmol) was then added dropwise. The reaction mixture was stirred at 0°C for 30 min and a further 4 h under reflux conditions. The flask was then cooled to 0°C and methanol (3 ml) was added to quench any excess borane. Subsequently, diethyl ether (10 ml) was added to precipitate the released polymeric sulfide. GC analysis of the organic layer showed the formation of benzyl alcohol (100%). The organic layer from the reaction was washed with brine (3 × 20 ml), and most of the solvent was removed under vacuum. Hexane (10 ml) and ether (10 ml) were added to the residue, which further precipitated the polymeric material. The polymer was filtered off and the filtrate was dried (MgSO₄). The solvent was removed under reduced pressure to give benzyl alcohol (0.45 g, 4.17 mmol, 83%) as a colorless oil identical to an authentic sample.

Acknowledgements

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