SHORT PAPER

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Highly stereoselective synthesis of *trans*-diaryl epoxides via semi-stabilised telluronium ylide†

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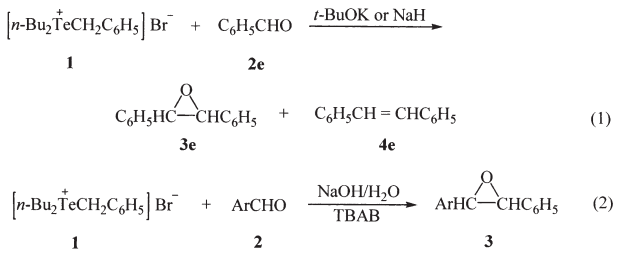
Benzyldibutyltelluronium bromide can react with LDA to form benzyldibutyltelluronium ylide ***in situ***, followed by the reaction with aromatic aldehydes, developed a novel method for the stereoselective synthesis of ***trans***-diaryl epoxides.

Keywords: *trans*-diaryl epoxides, telluronium ylide

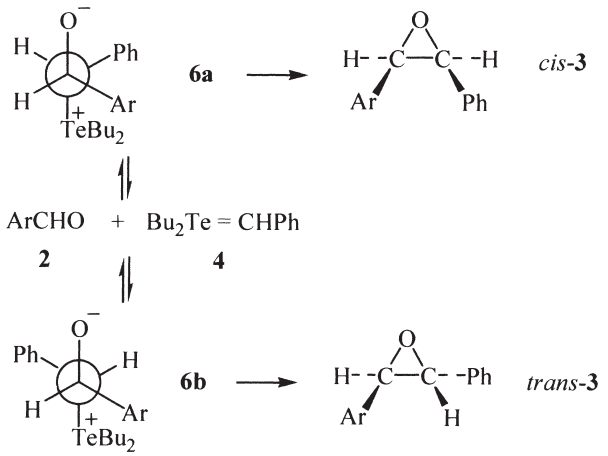
Recently more attentions have been paid in telluronium ylides and they have been widely applied in organic synthesis.[1] It was found in our lab that, stabilized telluronium ylides formed *in situ* can react with aldehydes to give α,β-unsaturated compounds in good yields.[2] In 1999, Huang *et al.* reported that allylic telluronium ylide formed *in situ* can react with aldehydes to give *cis*-α, β-unsaturated epoxides stereoselectively.[3] As the continuation of our research on telluronium ylides, we investigated on the application of benzyltelluronium ylide as a semi-stabilised telluronium ylide in organic synthesis.

We found that, in the presence of potassium *tert*-butoxide or sodium hydride, the benzyldibutyltelluronium bromide **1** could react with benzaldehyde **2e** to give the mixture of epoxide **3e** and alkene **4e** (eqn 1, Scheme 1). The ratio of epoxide **3e** to alkene **4e** is about 3 to 1. Then we utilised tetrabutylammonium bromide (TBAB) as a phase transfer catalyst and sodium hydroxide as a base and found the reaction of benzyldibutyltelluronium bromide **1** with aromatic aldehyde **2** can carried out smoothly to produce diaryl epoxides **3** in good yields (Method A) with *trans*-isomer predominance and no alkene was observed (eqn 2, Scheme 1).



Scheme 1

A possible mechanism is proposed to account for the formation of epoxides **3** and their *trans*-stereoselectivities (Scheme 1). Benzyltelluronium ylide **5** would undergo nucleophilic addition with aldehyde **2** to form betaine **6**, which exists two conformations in the anti-elimination for epoxide **3**. Owing to its less steric hindrance, betaine **6b** is a preferential intermediate contrast to betaine **6a**, followed by the anti-elimination to give *trans*-**3** stereoselectively.



Scheme 2

It should be noted that the stereoselectivities for the synthesis of the epoxides **3** by the method A are not high (Entry 1–3, Table 1). Some experimental results indicate that lithium salt has effects on the stereochemistry of the reaction occurred by ylide.[4] Thus we treated telluronium salt **1** with lithium diisopropylamide (LDA) at -78°C to form telluronium ylide **5** *in situ*, followed by the reaction with aromatic aldehyde **2** to give

Table 1 Stereoselective synthesis of *trans*-diaryl epoxide via benzyltelluronium ylide **5**

Entry	Method	R	Product	Reaction Time(hr)	Isolated Yield(%)[a]	*trans/cis* [b]
1	A	4-$NO_2C_6H_4$	**3a**	3	78[5] (3a)	65/35
2	A	C_6H_5	**3e**	8	81[6] (3e)	60/40
3	A	4-$CH_3C_6H_4$	**3f**	11	73[7] (3f)	70/30
4	B	4-$NO_2C_6H_4$	**3a**	4	93[5] (3a)	97/3
5	B	4-FC_6H_4	**3b**	5	85[8] (3b)	90/10
6	B	4-ClC_6H_4	**3c**	5	90[8] (3c)	92/8
7	B	4-BrC_6H_4	**3d**	6	92[8] (3d)	89/11
8	B	C_6H_5	**3e**	9	85[6] (3e)	95/5
9	B	4-$CH_3C_6H_4$	**3f**	12	84[7] (3f)	88/12
10	B	4-$CH_3OC_6H_4$	**3g**	18	76[9] (3g)	91/9

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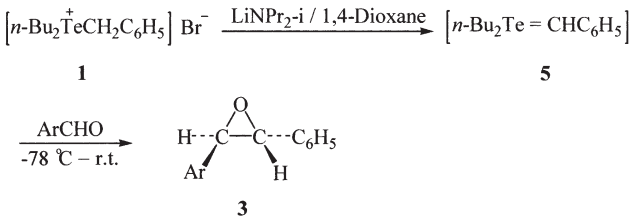
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

[a]All products are confirmed by ^{1}H NMR, IR and MS.

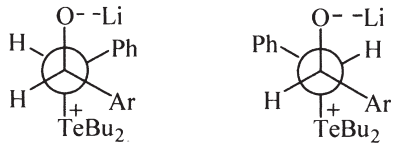
[b]The ratios of *trans*-epoxide to *cis*-epoxide are determined by ^{1}H NMR or GC.



Scheme 3

diaryl epoxide **3** in good yields (Method B). The *trans*-stereoselectivities of epoxides **3** are improved greatly, compared with the Method A (Table 1).

Due to the coordination of lithium cation with oxygen anion, the steric hindrance in conformation **7a** is increased more greatly than that in conformation **7b** (Scheme 4). So **7b** *vs* **7a** is more preferential than **6b** *vs* **6a** in *anti*-elimination and the *trans*-stereoselectivity is improved in the presence of lithium cation in Method B.



7a **7b**

Scheme 4

It is known to all that epoxides are important intermediate in organic synthesis. We developed a novel synthetic method (Method B) for the stereoselective synthesis of *trans*-diaryl epoxides **3** with the advantages of mild reaction conditions, simple procedures, good yields and high stereoselectivities.

Experimental

General procedure for the synthesis of diaryl epoxides **3** (*Method A*): To the solution of benzyldibutyltelluronium bromide **1** (0.78g, 2.0mmol) and TBAB (1mmol, 0.3g) in CH_2Cl_2 (10ml), was added dropwise the 10N aqueous solution of sodium hydroxide (20mmol, 2ml) at room temperature. After the reaction mixture was stirred for 10 min, the solution of aromatic aldehyde (2mmol) in CH_2Cl_2 (5ml) was added and the reaction mixture was stirred at room temperature for 3–11 h (Table 1). After filtration, the filtrate was concentrated and subjected to preparative TLC (silica gel, petroleum ether-ether as eluant) to give diaryl epoxides **3**.

General procedure for the stereoselective synthesis of trans-diaryl epoxides **3** (*Method B*): To the solution of benzyldibutyltelluronium bromide **1** (0.78g, 2.0mmol) in 1,4-dioxane (10ml), was added dropwise the solution of LDA (2.0mmol) in hexane (5ml) at –78°C. After the reaction mixture was stirred for 10 min, the solution of aromatic aldehyde **2** (2mmol) in THF (5ml) was added and the reaction mixture was warmed to room temperature gradually and stirred at this temperature for 4–18 h (Table 1). After filtration, the filtrate was concentrated and subjected to preparative TLC (silica gel, petroleum ether-ether as eluant) to give *trans*-diaryl epoxides **3**.

Selected ^{1}HNMR data, δ (CDCl$_3$): **3a**, *trans*: 8.26(2H, d, *J*=8.4 Hz), 7.53(2H, d, *J*=8.4 Hz), 7.47–7.27(5H, m), 3.99(1H, d, *J*=1.6 Hz), 3.87(1H, d, *J*=1.6 Hz); *cis*: 8.05(2H, d, *J*=8.8 Hz), 7.36(2H, d, *J*=8.8 Hz), 7.20–7.18(5H, m), 4.48(1H, d, *J*=4.0 Hz), 4.43(1H, d, *J*=4.4 Hz). **3e**, *trans*: 7.36–7.26(6H, m), 7.19(4H, d, *J*=8.4 Hz), 3.86(2H, d, *J*=1.6 Hz); *cis*: 7.31–7.22(6H, m), 7.05(4H, d, *J*=8.8 Hz), 4.47(2H, d, *J*=4.4 Hz). **3f**, *trans*: 7.37(2H, d, *J*=8.4 Hz), 7.27–7.06(5H, m), 6.98(2H, d, *J*=8.4 Hz), 3.86(1H, d, *J*=1.6 Hz), 3.74(1H, d, *J*=1.6 Hz), 2.35(3H, s); *cis*: 7.30(2H, d, *J*=8.8 Hz), 7.22–7.05(5H, m), 6.93(2H, d, *J*=8.8 Hz), 4.57(1H, d, *J*=4.4 Hz), 4.55(1H, d, *J*=4.4 Hz), 2.34(3H, s).

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