Convenient and Stereoselective Synthesis of Symmetrical (*E*)-Stilbenes via Homocoupling of 1,3-Dibenzylbenzotriazolium Bromides

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Abstract: Using NaH as the base and DMSO as the solvent, a series of symmetric (*E*)-stilbenes were prepared in good yields via the homocoupling of 1,3-dibenzylbenzotriazolium bromides at room temperature.

Key words: stilbenes, 1,3-dibenzylbenzotriazolium bromides, ylides, coupling, elimination

Benzotriazole is an inexpensive, stable, and versatile compound. It can act as a leaving group, proton activator, cation stabilizer, radical precursor, and anion precursor. Therefore, benzotriazole-based intermediates have proved to be important and efficient reagents in organic synthesis.¹ Benzotriazolium salts have also been prepared and reported.²⁻⁵ However, most of the reported benzotriazolium salts were investigated as cyclophanes² or ionic liquids.³ Although some publications have discussed the preparation and properties of benzotriazolium ylides,⁴ but very few have reported the reactions of benzotriazolium ylides.⁵ Pardo and co-workers obtained new stable betains from the reaction of 3-dicyanomethyl-1-ethylbenzotriazolium ylide with acetylenic esters.^{5a} It was interpreted that the new betains were formed by the [2+3] cycloaddition of 3-dicyanomethyl-1-ethylbenzotriazolium ylide with acetylenic esters followed by a subsequent ring-opening reaction. Gandasegui and co-worker investigated the reactions of 3-methyl-1-phenacylbenzotriazolium ylide with isocyanates or isothiocyanates, and they also obtained new betains.^{5b} More interestingly, it was reported that the dihydrofuran derivatives could be prepared from the reaction of 3-methyl-1-phenacylbenzotriazolium ylide with aldehyde.5c

Considering 1-substituted benzotriazoles are good leaving groups and benzotriazolium ylides are good nucleophiles, we tried to prepare the stilbenes from the homocoupling of 1,3-disubstituted benzotriazolium salts in the presence of base. As expected, 1,2-diphenylethene (**2a**) was isolated in good yield (Table 1, entry 1) from the reaction of 1,3-dibenzylbenzotriazolium bromide **1a** with KOt-Bu. In order to improve the yield of **2a**, the effect of the solvent and base was investigated. As shown in Table 1, using NaH as the base and DMSO as the solvent (entry 6), an excellent yield of 2a (91%) was obtained. However, the reactions in MeCN, THF, or *t*-BuOH produced 2a in low yields due to the poor solubility of 1a in these solvents. Using K₂CO₃ or Et₃N as the base, compound 2a was not obtained. This illustrated that the basicities of K₂CO₃ and Et₃N were not strong enough to generate benzotriazolium ylide at room temperature.

Table 1Homocoupling of 1,3-Dibenzylbenzotriazolium Bromide:Effects of Solvent and Base^a

Ph 2	Ph base r.t.	→ ^{Ph} → Ph + 2 c	
1a	l	2a	3a
Entry	Base	Solvent	Yield (%) ^b
1	KOt-Bu	DMSO	59
2	KOt-Bu	DMF	28
3	KOt-Bu	MeCN	39
4	KOt-Bu	THF	25
5	KOt-Bu	t-BuOH	10
6	NaH	DMSO	91
7	K ₂ CO ₃	DMSO	0
8	Et ₃ N	DMSO	0
9	n-BuLi	THF	19

^a Reaction conditions: 1,3-dibenzylbenzotriazolium bromide (1a, 3 mmol), base (6 mmol), solvent (6 mL), atmosphere, r.t.
 ^b Isolated yields.

Using NaH as the base and DMSO as the solvent, various 1,3-disubstituted benzotriazolium salts were used in the preparation of 1,2-diphenylethene (**2a**, Table 2). It was shown that the homocoupling of 1-benzyl-3-ethylbenzo-triazolium bromide also produced **2a** in high yield (Table 2, entry 4), but both 1-benzyl-3-methylbenzotriazolium bromide (Table 2, entry 2), and 1-benzyl-3-methylbenzotriazolium iodide (Table 2, entry 3) produced **2a** in lower yield. Styrene was found in the reaction mixtures by

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Table 2 Preparation of 1,2-Diphenylethene **2a** from Various 1,3-Disubstituted Benzotriazolium Salts^a

	NaH, DMSO	Ph	
Entry	R	Х	Yield (%) ^b
1	Bn	Br	91
2	Me	Br	56
3	Me	Ι	68
4	Et	Br	83
5	Ph	Br	trace

^a Reaction conditions: 1,3-disubstituted benzotriazolium salts (3 mmol), NaH (6 mmol), DMSO (6 mL), atmosphere, r.t.
 ^b Isolated yields.

GC-MS determination. However, it was still unclear why there were only small amounts of **2a** obtained in the homocoupling of 1-benzyl-3-phenylbenzotriazolium bromide (Table 2, entry 5).

Under the optimized conditions (Table 1, entry 6), a series of 1,3-dibenzylbenzotriazolium bromides were subjected to this reaction, which are listed in Table 3. In all these cases the desired stilbenes were obtained in good yields. It was found that both electron-donating and electron-withdrawing substituents on the aromatic ring of the benzyl group decreased the yield of stilbenes. In addition, *ortho, meta*, and *para* substituents on the aromatic ring of the benzyl group gave similar yields of stilbenes. More intriguingly, all reactions displayed high stereoselectivity and most of them only produced (E)-stillbenes (entries 1– 5 and 10).



Table 3 Preparation of Stilbenes from Various 1,3-Dibenzylbenzotriazolium Bromides^a

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Ar 2 1	$\frac{Br}{Ar}$ $\frac{NaH, DMSO}{r.t.}$ $Ar \rightarrow 2$ 2	$N \ge N$ $N \ge N$ $N \ge Ar$ 3		
Entry	1,3-Dibenzylbenzotriazolium bromides 1	Product 2	$E/Z^{\rm b}$	Yield (%) ^c
6		CI	90:10	59
7		2f Cl	86:14	57
	1g	2g		
8		CI-CI	98:2	61
	ີ ເ 1h	2h		
9	Br N-N, Br	BrBr	95:5	64
	Br 1i	2i		
10	F N N Br	F	100:0	65
	F 1j	2j		

 Table 3
 Preparation of Stilbenes from Various 1,3-Dibenzylbenzotriazolium Bromides^a (continued)

^a Reaction conditions: 1,3-dibenzylbenzotriazolium bromide 1 (3 mmol), NaH (6 mmol), DMSO (6 mL), atmosphere, r.t.

^b E/Z ratio was determined by GC-MS.

^c Isolated yields.

A possible mechanism is presented in Scheme 1, which is similar to the reported mechanism of homocoupling of arylmethyl phosphonium salts.⁶ First, 1,3-dibenzylbenzotriazolium ylide **A** is formed by the reaction of 1,3-dibenzylbenzotriazolium bromide with NaH. And then it reacts with another equivalent 1,3-dibenzylbenzotriazolium bromide to form the intermediate **B**. Finally, intermediate **B** undergoes a Hoffmann elimination to give stilbene **2**. The byproduct 1-benzylbenzotriazole **3** can be easily recovered by column chromatography.

Stilbenes are widely used as dyes, brighteners, whiteners of paper and textiles, and photobleachers due to their outstanding optical properties. Although they can be prepared by Wittig-type reactions,⁷ metal-catalyzed coupling

reactions,⁸ and homocoupling of arylmethyl phosphonium salts^{6,9} or aryl aldehyde tosylhydrazones,¹⁰ most of the reported synthetic methods suffer from the use of expensive and toxic materials, such as transition metals, phosphonium salts, and hydrazines. In this process, the starting materials 1,3-dibenzylbenzotriazolium bromides **1** are nontoxic, cheap, and easily available from the reaction of 1-benzylbenzotriazole with benzyl bromide.^{2d}

In conclusion, we have developed a novel, convenient, and efficient synthesis of symmetrical (E)-stilbenes by homocoupling of 1,3-dibenzylbenzotriazolium bromides. The advantages of this method are the use of cheap, non-toxic, easily available materials, mild reaction conditions, simple operations, and high stereoselectivity.



Scheme 1 Proposed mechanism of the homocoupling reaction

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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