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Original article Cycloaddition reactions of benzyne with olefins



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1. Introduction

Benzocyclobutenes are useful both as intermediates in the field of organic synthesis and as structural elements in active pharmaceutical compounds [1,2]. More importantly, they can undergo thermal electrocyclic ring-opening to give ortho-xylylenes that can then react in pericyclic reactions, such as Diels– Alder cycloadditions [3–5]. These characteristics have been fully exploited in the total synthesis of polycyclic natural products [1,2]. Although benzocyclobutenes possess high synthetic value themselves, hardly any general procedures exist for the preparation of functionalized benzocyclobutenes. This greatly restricts their availability and their use as organic synthesis intermediates.

The biaryl structural motif and 9,10-dihydrophenanthrene derivatives are dominant features and general structural units in many pharmaceutically important and biologically active compounds [6,7]. As a consequence, organic chemists have attempted to exploit new and more efficient aryl–aryl bond-forming methods for over a century [8]. Despite the variety of routes that have been developed to synthesize aryl–aryl bonds, the most widespread methods are transition-metal-mediated reactions [9,10]. Hence, synthesizing biaryl compounds and 9,10-dihydrophenanthrene derivatives in the absence of a transition metal catalyst remains an important and significant project.

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ABSTRACT

Some novel cycloaddition reactions based on benzyne and olefins have been developed. These reactions were performed in the absence of a transition metal catalyst, and they displayed good yields. These cycloaddition reactions of benzyne with olefins provide effective routes for synthesizing benzocyclobutenes, biaryl compounds and 9,10-dihydrophenanthrene derivatives.

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Benzyne is an extremely reactive intermediate [11], and has been comprehensively used as a building block in organic synthesis [12]. Nevertheless, its application has been limited due to the strict reaction conditions for its preparation. With the emergence of moderate preparation methods of arynes [13], it has attracted a great deal of attention in the area of organic synthesis.

In this article, we report cycloaddition reactions of benzyne with olefins. These cycloaddition reactions provide effective routes for the synthesis of benzocyclobutenes, biaryl compounds and 9,10-dihydrophenanthrene derivatives in the absence of a transition metal catalyst. Moreover, these reactions display good yields.

2. Experimental

The benzyne precursor **1a** was prepared using the known procedures [13]. Commercially available CsF, norbornadiene, norbornene, vinyl butyl ether, methyl acrylate, ethyl acrylate, styrene, trans-stilbene, indene and all reagents were used without further purification. The ¹H NMR and ¹³C NMR spectra were acquired on American Varian Mercury Plus 400 spectrometer (400 MHz). The ¹H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constant (Hz). ¹³C NMR chemical shifts are reported in ppm (δ) relative to the central line of the triplet for CDCl₃ at 77 ppm. EI-MS was obtained using a Thermo Scientific DSQII. Elemental analyses (C, H) were performed by the Microanalytical Services, College of Chemistry, CCNU. The X-ray crystal-structure determinations of **1c**, **8c** and **9c** were obtained on

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a Bruker APEX DUO CCD system. Column chromatographic separations were carried out on silica gel (200–300 mesh). TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm.

2.1. General synthetic procedure for 1c

The mixture of o-(trimethylsilyl)phenyl triflate (3 mmol, 2.0 equiv.), norbornadiene (1.0 equiv.), and anhydrous CsF (6.0 equiv.) was soluted in dried CH₃CN (15 mL). Then, the resulting mixture was stirred at room temperature for 12 h. After the reaction completed, 20 mL of water was added to the mixture, and then extracted with CH₂Cl₂ (3×20 mL), and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether) to afford the desired product **1c**.

Compound **1c**: White solid, mp: 121.8–122.5 °C. ¹H NMR (400 MH_z, CDCl₃): δ 7.19 (t, 4H, *J* = 4 Hz), 7.01–6.99 (m, 4H), 3.29 (s, 4H), 2.38 (s, 2H), 0.76 (s, 2H). ¹³C NMR (100 MH_z, CDCl₃): δ 146.36, 127.32, 121.96, 49.41, 37.28, 26.04. EI-MS: *m*/*z* 244 [M]⁺. Anal. Calcd. for C₁₉H₁₆: C, 93.40; H, 6.60. Found: C, 93.48; H, 6.55.

2.2. General synthetic procedure for 2c

The mixture of *o*-(trimethylsilyl)phenyl triflate (1 mmol, 1.0 equiv.), norbornadiene (2.0 equiv.), and anhydrous CsF (3.0 equiv.) was soluted in dried CH₃CN (15 mL). Then, the resulting mixture was stirred at room temperature for 12 h. After the reaction completed, 20 mL of water was added to the mixture, and then extracted with CH₂Cl₂ (3×20 mL), and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether) to afford the desired product **2c**.

Compound **2c**: Colorless oil. ¹H NMR (400 MH_z, CDCl₃): δ 7.20–7.15 (m, 2H), 7.09–7.05 (m, 2H), 6.24 (d, 2H, *J* = 12 Hz), 3.15 (t, 2H, *J* = 10 Hz), 2.78 (s, 2H), 1.27 (t, 1H, *J* = 8 Hz), 0.87 (d, 1H, *J* = 8 Hz). ¹³C NMR (100 MH_z, CDCl₃): δ 146.13, 136.66, 127.00, 121.77, 47.55, 41.54, 41.34, 29.70. EI-MS: *m*/*z* 168 [M]⁺. Anal. Calcd. for C₁₃H₁₂: C, 92.81; H, 7.19. Found: C, 92.85; H, 7.12.

2.3. General synthetic procedures for **3c–6c**

The mixture of o-(trimethylsilyl)phenyl triflate (3 mmol, 2.0 equiv.), olefins (1.0 equiv.), and anhydrous CsF (6.0 equiv.) was soluted in dried CH₃CN (15 mL). The resulting mixture was stirred at room temperature for 12 h. After the reaction completed, 20 mL of water was added to the mixture, and then extracted with CH₂Cl₂ (3×20 mL), and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether) to afford the desired products **3c–6c**.

Compound **3c**: Colorless oil. ¹H NMR (400 MH_z, CDCl₃): δ 7.20–7.18 (m, 2H), 7.00–6.98 (m, 2H), 3.18 (s, 2H), 2.27 (s, 2H), 1.60–1.55 (m, 2H), 1.18 (d, 2H, *J* = 4 Hz), 0.97–0.94 (m, 1H), 0.85 (d, 1H, *J* = 8 Hz). ¹³C NMR (100 MH_z, CDCl₃): δ 146.50, 127.11, 121.81, 50.44, 36.57, 31.92, 27.79. EI-MS: *m/z* = 170 [M]⁺. Anal. Calcd. for C₁₃H₁₄: C, 91.71; H, 8.29. Found: C, 91.65; H, 8.33.

Compound **4c**: Colorless oil. ¹H NMR (400 MH_z, CDCl₃): δ 7.28–7.23 (m, 2H), 7.14 (d, 2H, *J* = 8 Hz), 5.04 (s, 1H), 3.66–3.57 (m, 2H), 3.48–3.44 (m, 1H), 3.12 (d, 1H, *J* = 12 Hz), 1.65–1.57 (m, 2H), 1.44–1.39 (m, 2H), 0.94 (t, 3H, *J* = 6 Hz). ¹³C NMR (100 MH_z, CDCl₃): δ 146.30, 142.54, 129.18, 126.91, 123.44, 122.70, 68.63, 38.63, 31.95, 19.37, 13.90. El-MS: *m*/*z* 176 [M]⁺. Anal. Calcd. for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.81; H, 9.09.

Compound **5c**: Light yellow oil. ¹H NMR (400 MH_z, CDCl₃): δ 7.26–7.24 (m, 2H), 7.18 (d, 1H, *J* = 4 Hz), 7.11 (d, 1H, *J* = 4 Hz), 4.32

(t, 1H, *J* = 4 Hz), 3.73 (d, 3H, *J* = 8 Hz), 3.48 (d, 2H, *J* = 4 Hz). These data are in good agreement with literature values [14].

Compound **6c**: Light yellow oil. ¹H NMR (400 MH_z, CDCl₃): δ 7.26–7.23 (m, 2H), 7.18 (d, 1H, *J* = 4 Hz), 7.10 (t, 1H, *J* = 8 Hz), 4.30 (t, 1H, *J* = 4 Hz), 4.22–4.17 (m, 2H), 3.47 (t, 2H, *J* = 4 Hz), 1.32–1.27 (m, 3H). ¹³C NMR (100 MH_z, CDCl₃): δ 171.94, 144.01, 142.71, 127.91, 127.09, 122.67, 122.23, 60.58, 45.74, 33.68, 14.04. EI-MS: *m/z* 176 [M]⁺. Anal. Calcd. for C₁₁H₁₂O₂: C, 74.98; H, 6.86. Found: C, 74.91; H, 6.91.

2.4. General synthetic procedure for 7c

The mixture of *o*-(trimethylsilyl)phenyl triflate (1.5 mmol, 3.0 equiv.), styrene (1.0 equiv.), and anhydrous CsF (9.0 equiv.) was soluted in dried 1,4-dioxane (5 mL). Then, the resulting mixture was stirred at 110 °C for 12 h. After the reaction completed, 20 mL of water was added to the mixture and then extracted with CH₂Cl₂ (3 × 20 mL), and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/CH₂Cl₂) to afford the desired product **7c**.

Compound **7c**: Light yellow oil. ¹H NMR (400 MH_z, CDCl₃): δ 7.75 (d, 2H, *J* = 8 Hz), 7.32–7.27 (m, 3H), 7.24 (d, 3H, *J* = 4 Hz), 2.89 (d, 4H, *J* = 12 Hz). ¹³C NMR (100 MH_z, CDCl₃): δ 137.13, 134.30, 127.99, 127.22, 126.82, 123.56, 28.88. EI-MS: *m/z* 180 [M]⁺. Anal. Calcd. for C₁₄H₁₂: C, 93.29; H, 6.71. Found: C, 93.25; H, 6.76.

2.5. General synthetic procedure for 8c

The mixture of o-(trimethylsilyl)phenyl triflate (3 mmol, 3.0 equiv.), trans-stilbene (1.0 equiv.), and anhydrous CsF (9.0 equiv.) was soluted in dried CH₃CN (15 mL). Then, the resulting mixture was stirred at room temperature for 12 h. After the reaction completed, 20 mL of water was added to the mixture, and then extracted with CH₂Cl₂ (3× 20 mL), and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/CH₂Cl₂) to afford the desired product **8c**.

Compound **8c**: White solid, mp: 165.8–166.6 °C. ¹H NMR (400 MH_Z, CDCl₃): δ 7.91 (d, 2H, *J* = 8 Hz), 7.36–6.96 (m, 16 H, aryl-H), 4.43 (s, 2H). ¹³C NMR (100 MH_Z, CDCl₃): δ 143.77, 137.06, 134.25, 129.95, 128.29, 128.13, 128.03, 127.54, 126.26, 123.52, 52.59. EI-MS: *m/z* 332 [M]⁺. Anal. Calcd. for C₂₆H₂₀: C, 93.94; H, 6.06. Found: C, 93.99; H, 6.02.

2.6. General synthetic procedure for 9c

The mixture of o-(trimethylsilyl)phenyl triflate (3 mmol, 3.0 equiv.), indene (1.0 equiv.), and anhydrous CsF (9.0 equiv.) was soluted in dried CH₃CN (15 mL). Then, the resulting mixture was stirred at room temperature for 12 h. After the reaction completed, 20 mL of water was added to the mixture, and then extracted with CH₂Cl₂ (3×20 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/CH₂Cl₂) to afford the desired product **9c**.

Compound **9c**: White solid, mp: 89.7–90.6 °C. ¹H NMR (400 MH_z, CDCl₃): δ 7.27–7.18 (m, 4H), 7.13–7.06 (m, 4H), 6.41–6.37 (m, 1H), 6.11 (d, 1H, *J* = 8 Hz), 5.98–5.95 (m, 1H), 5.88 (d, 1H, *J* = 8 Hz), 3.34 (d, 2H, *J* = 20 Hz), 1.83 (d, 1H, *J* = 8 Hz), 1.64–1.61 (m, 1H). ¹³C NMR (100 MH_z, CDCl₃): δ 148.56, 145.94, 143.91, 142.76, 131.37, 128.24, 127.80, 127.69, 127.57, 125.88, 125.00, 124.32, 122.01, 121.59, 121.43, 120.95, 60.21, 52.79, 52.51, 45.68, 45.44. EI-MS: *m/z* = 268 [M]⁺. Anal. Calcd. for C₂₁H₁₆: C, 93.99; H, 6.01. Found: C, 93.91; H, 6.06.

Table 1

Optimization of [2+2] cycloaddition reaction of benzyne with norbornadiene^a



^a Reactions performed on 0.5 mmol scale, 5 mL of the solvent.

^b Isolated yield.

3. Results and discussion

We initially examined the [2+2] cycloaddition reaction of benzyne and norbornadiene using 2.0 equiv. of compound 1a, 2.0 equiv. of 1b and 2.0 equiv. of CsF at 25 °C in anhydrous acetonitrile (see Table 1, entry 1), the desired [2 + 2] cycloaddition product 1c was obtained in a yield of 17%. In addition, we were able to grow a single crystal of 1c, and its structure was confirmed by Xray crystallography (Fig. 1a). Subsequently, we altered the molar ratio of the reactants and, as shown in Table 1, a higher yield was observed when the proportion of **1b** was reduced from 2.0 to 1.0 equiv. (Table 1, entry 2). Increasing yields were also obtained when we increased the amount of CsF (Table 1, entries 3-4). Further studies concentrated on the effect of temperature. Data in Table 1 (entries 5 and 6) show that the reaction is less effective at higher temperatures. Therefore, the best result (75% yield of [2+2])cycloaddition reaction product 1c) was obtained using 1a (2.0 equiv.), 1.0 equiv. of 1b, 6.0 equiv. of CsF in acetonitrile at 25 °C for 12 h.

Using this optimized set of reaction conditions, we then tested other [2+2] cycloaddition reactions of benzyne and olefins (Table 2). It was determined that other olefin substrates, including norbornene **2b**, vinyl butyl ether **3b**, methyl acrylate **4b**, ethyl acrylate **5b**, could also smoothly undergo a [2+2] cycloaddition reaction with yields ranging from 78% to 85% (Table 2, entries 3–6). In addition, we obtained the product **2c** involving a single double bond [2+2] cycloaddition reaction of benzyne and norbornadiene in a yield of 73% using 1.0 equiv. **1a**, 2.0 equiv. **1b** and 3.0 equiv. CsF at 25 °C in anhydrous acetonitrile (Table 2, entry 2).

Next, biaryl compound **7c** was obtained when we carried out the reaction of benzyne with styrene using 3.0 equiv. of **1a**,

Table 2

[2+2] Cycloaddition reaction products of benzyne with olefins.^a



^a Reaction conditions: *o*-(trimethylsilyl)phenyl triflate (2.0 equiv., 3.0 mmol), olefin (1.0 equiv.), CsF (6.0 equiv.), CH₃CN, 25 °C, 12 h.

^b Isolated yields.

 $^{\rm c}\,$ o-(Trimethylsilyl)phenyl triflate (1.0 equiv., 1.0 mmol), olefin (2.0 equiv.), CsF (3.0 equiv.), CH_3CN, 25 $^{\circ}$ C, 12 h.



Scheme 1. Cycloaddition reactions of benzyne with trans-stilbene.

3.0 equiv. of **6b** and 9.0 equiv. of CsF at 25 °C in anhydrous acetonitrile (Table 3, entry 1). Subsequently, we attempted to optimize the molar ratios of the reactants. As can be seen in Table 3, increasing yields were observed as the quantity of **1b** was reduced from 3.0 equiv. to 1.5 equiv., then to 1.0 equiv. under the same conditions (Table 3, entries 2–3). Subsequent studies focused on the effects of solvent and temperature. Entries 4–7 of Table 3 demonstrate that the best reaction condition used dioxane as solvent. Simultaneously, we also noticed that higher temperatures produced increasing yields (Table 3, entries 8–9). According to the above optimizations, the best result (87% yield of the biaryl



Fig. 1. The single crystal structure of compound 1c (a), 8c (b) and 9c (c) (hydrogen atoms are omitted for clarity).



Scheme 2. Proposed mechanism of the reaction.



Scheme 3. Cycloaddition reactions of benzyne with indene.

compound **7c**) was obtained using **1a** (3.0 equiv.), 1.0 equiv. of **6b**, 9.0 equiv. of CsF at 110 °C in anhydrous dioxane.

In later work, we obtained the remarkable cycloaddition product 8c in 62% vield when we examined the reaction of benzvne and trans-stilbene using 3.0 equiv. of **1a**, 1.0 equiv. of **7b** and 9.0 equiv. of CsF at 25 °C in anhydrous acetonitrile (Scheme 1). The possible mechanism for this reaction is shown in Scheme 2. The [2 + 4] cycloaddition reaction of trans-stilbene with benzyne generated from o-(trimethylsilyl)phenyl triflate resulted in the generation of intermediate 1, which can add to another molecule of electrophilic benzyne in a concerted-ene reaction leading to the formation of the target product. However, the [2 + 4] cycloaddition reaction of *cis*-stilbene with benzyne can not be carried out due to the presence of the space steric hindrance. Therefore, we were not able to obtain the corresponding cycloaddition product under the same reaction conditions using cis-stilbene as substrate. The structure of compound 8c was determined by X-ray crystallography (Fig. 1b).

Finally, the reaction of benzyne and indene was investigated, and product **9c** was obtained in a yield of 95% with 3.0 equiv. of **1a**,

Table 3

Optimization of [2+4] cycloaddition reaction of benzyne with styrene^a

	MS + -	CsF		
1a	6b		7c ~	
Entry	Molar ratio of 1a/6b /CsF	Temp (°C)	Solvent	7c Yield ^b

1	3/3/9	25	CH ₃ CN	15%
2	3/1.5/9	25	CH ₃ CN	21%
3	3/1/9	25	CH ₃ CN	25%
4	3/1/9	25	THF	31%
5	3/1/9	25	Dioxane	51%
6	3/1/9	25	DCM	NR ^c
7	3/1/9	25	DCE	NR ^c
8	3/1/9	50	Dioxane	58%
9	3/1/9	110	Dioxane	87%

^a Reactions performed on 0.5 mmol scale, 5 mL of the solvent.

^b Isolated yield.
 ^c NR: No reaction.

1.0 equiv. of **8b** and 9.0 equiv. of CsF at 25 °C in anhydrous acetonitrile (Scheme 3). The synthesis of product **9c** is the result of a [2 + 4] cycloaddition and then [2 + 2] cycloaddition reaction of benzyne. The structure of compound **9c** has also been determined by X-ray crystallography (Fig. 1c).

4. Conclusion

In summary, some novel and significant cycloaddition reactions and products based on the reactions of benzyne and olefins have been developed. These cycloaddition reactions display good yields, even in the absence of a transition metal catalyst. These reactions of benzyne with olefins provide efficient methods for the synthesis of benzocyclobutenes, biaryl compounds and 9,10-dihydrophenanthrene derivatives.

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