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A Phosphine-Catalyzed Regioselective [3+2] Cycloaddition of Ethyl 5,5-Diarylpenta-2,3,4-trienoate with Aromatic Aldehydes and α,β-Unsaturated Carbonyl Compounds

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Abstract: Tributylphosphine-catalyzed regioselective [3+2] cycloadditions between ethyl 5,5-diarylpenta-2,3,4-trienoate **1** and various aromatic aldehydes **2** to produce a wide variety of polysubstituted 2,5-dihydrofurans **3**, and between **1** and β-unsubstituted α,β-unsaturated carbonyl compounds **5** to give polysubstituted cyclopentenes **6** with a quaternary carbon center, are reported. In both cases the reaction partners approach each other *via* the sterically less hindered orientation to afford the target products in excellent regioselectivity. The reaction mechanism involved first the generation of a zwitterionic intermediate between the butatriene **1** and PBu_3. For the formation of 2,5-dihydrofurans **3**, the preferred cyclization mode encompassed the nucleophilic attack of the α-position of butatriene to the aldehydic carbon of **2**, followed by the ring closure between the aldehydic oxygen of **2** and the γ-position of butatriene, which is the first report of a normal [3+2] cycloaddition between cumulenes and aldehydes. For the formation of cyclopentenes **6**, the reaction involved attack of the γ-position of the butatriene to the electron-deficient β-position of the α,β-unsaturated carbonyl compounds **5**, followed by the ring closure between the α-position of **5** and the α-position of butatriene, which shows a different regioselectivity to the previously reported [3+2] cycloadditions between butatriene and olefins.

Keywords: butatrienes; cycloaddition; phosphine catalysis; regioselectivity

Introduction

Cumulenes have attracted much attention in organic chemistry because the cumulated C=C double bonds exhibited some very interesting and unique reactivities. For example, they can serve as nucleophiles, electrophiles and dienophiles in many different classes of reactions.[1] Among the various types of cumulenes, allenes have been demonstrated as extremely useful reaction substrates as they often showed excellent regio- and stereoselectivities when employed in many reactions.[1a] Some allene derivatives have also been employed in the synthesis of natural products and materials.[2] Compared with allenes, butatrienes may possess an even richer chemistry and interesting reactivity due to the presence of an extra double bond functionality. Indeed, several research works on the synthesis and reactivity of butatrienes derivatives have already appeared in the literature.[3]

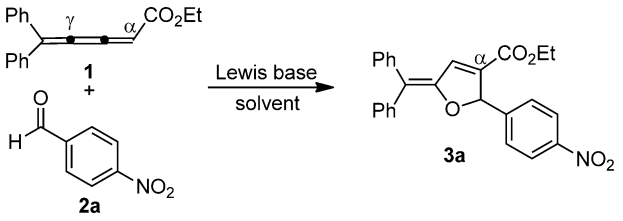
The phosphine-catalyzed [3+2] cycloaddition, developed by Lu in 1995,[4] is considered to be one of the most important reactions for cumulenes. For the reaction between allenic substrates and electron-deficient olefins, the reaction products are five-membered carbocycles with a quaternary stereogenic center.[5] This motif is also an important structural skeleton found in many natural products and bioactive molecules.[6] Alternatively, allenes could also react with aldehydes to produce dioxanes, pyrones, dihydropyrone, 1,3-dienes, or vinylcyclopropanes, and with ketones to construct dihydrofurans,[7] but there is only one example of γ-alkyl allenates with aryl aldehydes giving tetrahydrofurans, in which the γ-methyl or methylene was directly involved in the carbon-carbon bond-forming steps,[7g] rather than the normal [3+2] cycloaddition.

For similar reactions involving butatrienes, there is only one report in the literature. Shi disclosed the synthesis of five-membered carbocycles or pyrrolines *via* phosphine-mediated [3+2]cycloadditions between ethyl 5,5-diarylpenta-2,3,4-trienoates **1** and β-substituted conjugated olefins or *N*-tosylimines, respectively.[3g] It was noted that these products were formed from α-attack of the butatrienes to the β-position of the electron-deficient conjugated olefins, or the α-position of *N*-tosylimines. Herein, we wish to report two new reaction modes in the [3+2]cycloaddition reactions involving ethyl 5,5-diphenylpenta-2,3,4-trienoate **1**. First, the phosphine-catalyzed reaction between butatriene **1** and aromatic aldehydes **2** afforded furan derivatives – the normal [3+2]cycloaddition products resulting from the α-attack of the butatriene to the aldehydic carbon. Second, butatriene **1** reacted with β-unsubstituted α,β-unsaturated carbonyl compounds **5** to produce five-membered carbocycles **6**. The reaction course was originated from γ-attack of the butatriene to the β-position of the conjugated ester or ketone as the main product. This work further highlights the rich chemistry of butatriene compounds and their versatility in the construction of complex organic structures.

Results and Discussion

Initial experimentation with ethyl 5,5-diphenylpenta-2,3,4-trienoate (**1**) and *para*-nitrobenzaldehyde (**2a**) in the presence of tributylphosphine in THF at 60 °C led to the formation of a normal [3+2]cycloaddition adduct **3a** in very low yield (Table 1, entry 1). The reaction parameters were then adjusted in order to identify the optimal conditions for the [3+2]cycloaddition reaction. Fortunately, when the reaction was carried in $CHCl_3$ at 50 °C, a furan derivative **3a** was obtained in 66% yield (Table 1, entry 2). Thus, using $CHCl_3$ as the solvent, various phosphine catalysts (50 mol%) were employed as the promotors, it was found that tributylphosphine (PBu_3), dimethylphenylphosphine ($PPhMe_2$), methyldiphenylphosphine (PPh_2Me), and triphenylphosphine (PPh_3) (entries 2–5) could all catalyze the reaction, but the yield of the product was the highest with the use of PBu_3. This result implied that the nucleophilicity of the phosphines had a significant influence on the outcome of the reaction. Accordingly, a nitrogen-containing Lewis base such as triethylamine (Et_3N) was also tried, but no reaction occurred under the same conditions (entry 6). Using PBu_3 (50 mol%) as the optimized catalyst, the solvent effects were then explored (entries 1, 2, 7–11), all the reactions were carried out below the reflux temperature of the solvent. Compared with THF, toluene, CH_3CN, DMF, DCM, and CCl_4, $CHCl_3$ was the best reaction solvent in which

Table 1. Optimization of conditions of the [3+2]cycloaddition of **1** and **2a**.



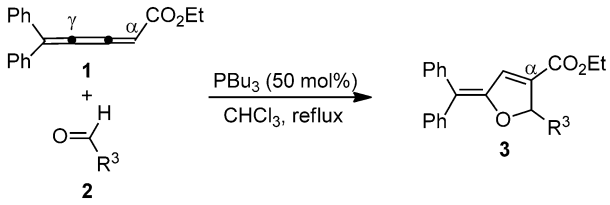
Entry[a]	Lewis base	Solvent	Temp. [°C]	Time [h]	Yield [%][b]
1	PBu_3	THF	60	10	10
2	PBu_3	$CHCl_3$	50	2[c]	66
3	$PPhMe_2$	$CHCl_3$	50	10	42
4	PPh_2Me	$CHCl_3$	50	10	36
5	PPh_3	$CHCl_3$	50	10	31
6	Et_3N	$CHCl_3$	50	10	NR
7	PBu_3	toluene	80	10	51
8	PBu_3	CH_3CN	30	10	43
9	PBu_3	DMF	60	2[c]	NR
10	PBu_3	DCM	30	10	34
11	PBu_3	CCl_4	60	20	NR
12	PBu_3	$CHCl_3$	30	10	46
13	PBu_3	$CHCl_3$	reflux	2[c]	68

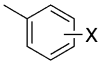
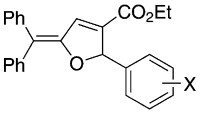
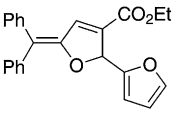
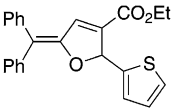
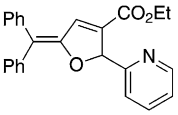
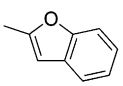
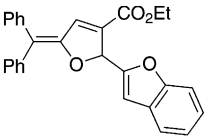
[a] All reactions were carried out with **1** (28 mg, 0.1 mmol) and **2a** (15 mg, 0.1 mmol) in the presence of Lewis base (50 mol%) in solvent (2.0 mL) under an argon atmosphere.
[b] Isolated yields.
[c] The reaction time was determined by the consumption of **1**.

the product **3a** was obtained in 66% yield (entry 2). When the reaction was performed at a higher temperature (refluxing $CHCl_3$), **3a** was formed in a slightly improved yield of 68% (entry 13). Hence the use of 50% mol of PBu_3 in refluxing $CHCl_3$ was determined to be the optimized reaction conditions.

Under the optimized reaction conditions, we set out to examine the scope and limitations of this reaction using **1** as the substrate with various aromatic aldehydes in the presence of PBu_3 (50 mol%) in refluxing $CHCl_3$ (Table 2). When the aromatic aldehydes possessed an electron-withdrawing substituent at the *para* or *meta* position of the aromatic ring, the reactions were found to proceed smoothly and the products **3** were obtained in moderate to good (64–84%) yields (entries 1–4). When the electron-withdrawing groups were introduced at the *ortho* position of the aromatic ring, the reaction time was longer and the corresponding products were obtained in moderate (40–48%) yields (entries 5 and 6). On increasing the number of the electron-withdrawing substituents at the aromatic ring, there was a little improvement of the yield (entry 7). But using benzaldehyde as the substrate resulted in a low yield (entry 8). When het-

Table 2. Scope of the PBu_3-mediated [3+2] cycloaddition of **1** and **2**.

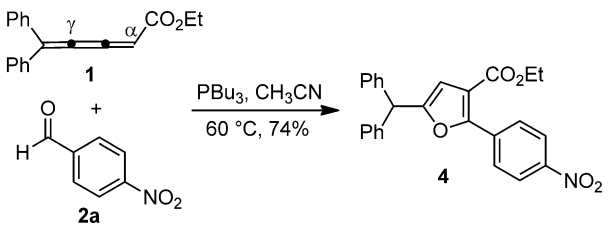


Entry[a]	2	R^3	Time [h]	3	Product	Yield [%][b]
						
1	**2b**	X = *p*-Br	2[c]	**3b**		64
2	**2c**	X = *p*-CN	2[c]	**3c**		80
3	**2d**	X = *p*-CF_3	2[c]	**3d**		84
4	**2e**	X = *m*-Br	2[c]	**3e**		67
5	**2f**	X = *o*-Br	10	**3f**		40
6	**2g**	X = *o*-NO_2	10	**3g**		48
7	**2h**	X = 2,4-dichloro	2[c]	**3h**		73
8	**2i**	X = H	10	**3i**		28
9	**2j**		2[c]	**3j**		64
10	**2k**		10	**3k**		60
11	**2l**		2[c]	**3l**		72
12	**2m**		2[c]	**3m**		82

[a] All reactions were carried out with **1** (28 mg, 0.1 mmol) and **2** (0.1 mmol) in the presence of PBu_3 (50 mol%) in $CHCl_3$ (2.0 mL) under an argon atmosphere.
[b] Isolated yields.
[c] The reaction time was determined by the consumption of **1**.

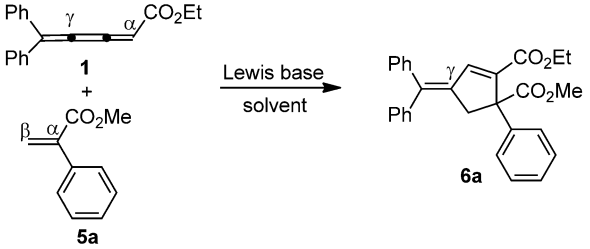
eroaromatic aldehydes were employed, the reaction also proceeded smoothly to afford **3** in good to excellent (60–82%) yields (entries 9–12). Interestingly, when the reaction solvent was switched to CH_3CN at 60 °C, a polysubstituted furan **4** was formed in 74% yield (Scheme 1). The structure of compound **4** was confirmed by ^1H and ^{13}C NMR, HMBC, and HR-MS analyses. When a solution of **3a** in CH_3CN was stirred at 60 °C with or without PBu_3 as catalyst, neither of them generated **4**. The furan derivative **4** was presumably formed directly from starting material **1** by cycloaddition–isomerization, which might be more thermodynamically stable compared to **3a**. However, no furan product was formed when other substrates **2b**–**2m** were subjected to the same reaction conditions, and only **3b**–**3m** were recovered unchanged.

The reaction was also examined with butatriene **1** and methyl 2-phenylacrylate (**5a**) in the presence of tributylphosphine in THF at 60 °C, a cyclopentene derivative **6a** was obtained in 65% yield (Table 3, entry 1). The reaction parameters were then adjusted in order to identify the optimal conditions for the



Scheme 1. Synthesis of compound **4**.

Table 3. Optimization of conditions of the [3+2] cycloaddition of **1** and **5a**.



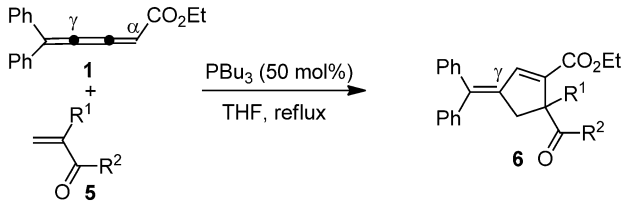
Entry[a]	Lewis base [mol%]	Solvent	Temp. [°C]	Time [h]	Yield [%][b]
1	PBu_3 (50)	THF	60	3[c]	65
2	PMe_3 (50)	THF	60	1[c]	55
3	$PPhMe_2$ (50)	THF	60	10[c]	55
4	PPh_2Me (50)	THF	60	10[c]	36
5	PPh_3 (50)	THF	60	20	NR
6	$HPPh_2$ (50)	THF	60	20	NR
7	Et_3N (50)	THF	60	20	NR
8	PBu_3 (50)	DCE	60	10[c]	30
9	PBu_3 (50)	toluene	60	10[c]	48
10	PBu_3 (50)	CH_3CN	60	2[c]	40
11	PBu_3 (50)	DMF	60	2[c]	58
12	PBu_3 (50)	DCM	35	10[c]	45
13	PBu_3 (50)	1,4-dioxane	60	4[c]	56
14	PBu_3 (30)	THF	60	20	57
15	PBu_3 (80)	THF	60	3[c]	67
16	PBu_3 (50)	THF	reflux	2[c]	72

[a] All reactions were carried out with **1** (28 mg, 0.1 mmol) and **5a** (16 mg, 0.1 mmol) in the presence of a Lewis base in solvent (2.0 mL) under an argon atmosphere.
[b] Isolated yields.
[c] The reaction time was determined by the consumption of **1**.

[3+2] cycloaddition reaction. Using THF as the solvent, other phosphine compounds such as trimethylphosphine (PMe_3), $PPhMe_2$, PPh_2Me were also examined, but in all cases lower yields were obtained (entries 2–4). On the other hand, electron-deficient phosphines such as PPh_3 and diphenylphosphine ($HPPh_2$), and a nitrogen-containing Lewis base Et_3N could not promote the reaction (entries 5, 6, and 7). With the choice of PBu_3 as the catalyst, a further survey of conditions indicated that THF was the best solvent as compared with DCE, toluene, CH_3CN, DMF, DCM, and 1,4-dioxane (entries 8–13). Meanwhile, the effects of the amount of PBu_3 and the reaction temperature were examined. Using less PBu_3 (30 mol%) resulted in a slowing down of the reaction and a decrease of the product yield of **6a**, and increasing the amount of the catalyst (80 mol%) resulted in little improvement of yield (entries 14 and 15). In addition, the reaction gave a slightly improved yield of **6a** when it was carried out in refluxing THF (entry 16). Thus, the cycloaddition was best conducted in refluxing THF in the presence of 0.5 equiv. of PBu_3.

After optimizing the reaction conditions, we then examined the substrate scope of the reaction between compound **1** and a variety of β-unsubstituted conjugated olefins **5** (Table 4). Similar to the case observed with aromatic aldehydes, when α-aryl α,β-unsaturated esters **5** (R^1 = Ar, R^2 = OR) with an electron-withdrawing substituent introduced at the *para* or *meta* position of the α-aryl ring were used as the substrates, the reactions proceeded very fast and the products **6** were obtained in excellent (84–91%) yields (entries 1, 2, 6, and 7). For substrates **5** (R^1 = Ar) bearing an electron-donating substituent at the *para* position of the α-aryl ring, the reaction time was longer and the corresponding adducts were obtained in moderate (52–61%) yields (entries 3–5). On the other hand, when the substituent was located at an *ortho*-position

Table 4. Scope of the PBu_3-mediated [3+2] cycloaddition of **1** and **5**.



Entry[a]	R^1	R^2	Time [h]	Product, Yield [%][b]
1	*p*-ClC_6H_4	OMe	2[c]	**6b**, 85
2	*p*-BrC_6H_4	OMe	2[c]	**6c**, 88
3	*p*-MeC_6H_4	OMe	8	**6d**, 61
4	*p*-*t*-BuC_6H_4	OMe	8	**6e**, 52
5	*p*-$MeOC_6H_4$	OMe	8	**6f**, 53
6	*m*-BrC_6H_4	OMe	2[c]	**6g**, 84
7	*m*-$CF_3C_6H_4$	OMe	2[c]	**6h**, 91
8	*o*-ClC_6H_4	OMe	8	**6i**, 32
9	*o*-$NO_2C_6H_4$	OMe	8	**6j**, 55
10	*p*-BrC_6H_4	OC_6H_5	2[c]	**6k**, 83
11[d]	C_6H_5	C_6H_5	5	**6l**, 55
12	*p*-ClC_6H_4	C_6H_5	2[c]	**6m**, 78
13	C_6H_5	*p*-BrC_6H_4	2[c]	**6n**, 75
14	C_6H_5	*p*-$MeOC_6H_4$	2[c]	**6o**, 40
15	*p*-ClC_6H_4	*p*-ClC_6H_4	2[c]	**6p**, 88
16	*p*-ClC_6H_4	*p*-$MeOC_6H_4$	2[c]	**6q**, 64
17	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	2[c]	**6r**, 34
18	*p*-ClC_6H_4	*n*-propyl	2[c]	**6s**, 58
19	H	OMe	3[c]	**6t**, 72
20	H	OEt	3[c]	**6u**, 60
21	H	O-*n*-Bu	3[c]	**6v**, 64
22	H	O-*t*-Bu	3[c]	**6w**, 62
23	H	Ocyclohexyl	3[c]	**6x**, 64

[a] All reactions were carried out with **1** (28 mg, 0.1 mmol) and **5** (0.1 mmol) in the presence of PBu_3 (50 mol%) in THF (2.0 mL) under argon atmosphere.
[b] Isolated yields.
[c] The reaction time was determined by the consumption of **1**.
[d] This reaction was carried out at 40 °C.

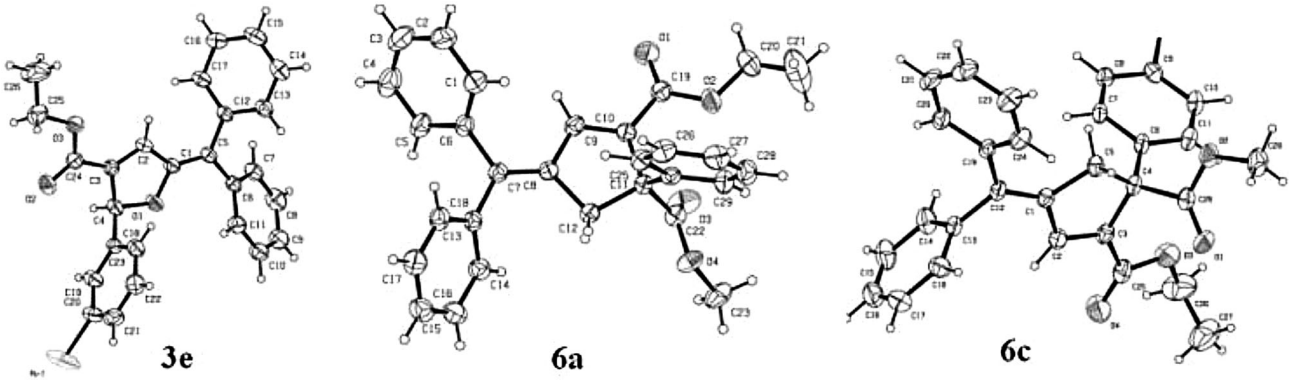


Figure 1. X-ray crystallographic structures of compounds **3e**, **6a**, and **6c**.

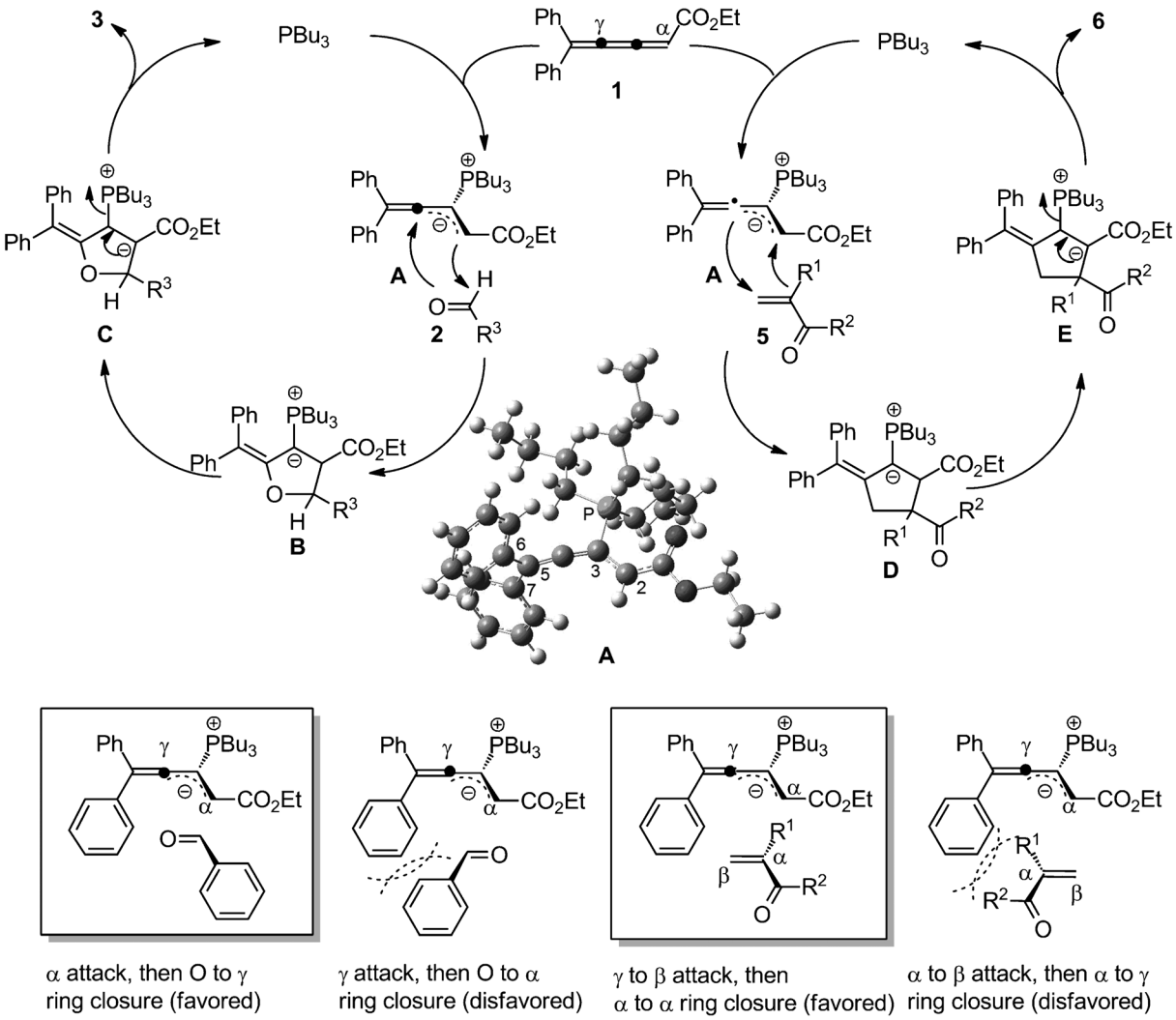
in the α-aryl ring, the corresponding products **6** were obtained in lower (32% and 55%) yields (entries 8 and 9). This may presumably be due to the steric blocking effect of the *ortho* substituent. Switching the ester functionality of **5** from methyl ester to phenyl ester showed little influence on the reaction (entries 2 *vs.* 10).

Ethyl 5,5-diphenylpenta-2,3,4-trienoate **1** could also react with β-unsubstituted α,β-unsaturated ketones **5** (R^1 = Ar, R^2 = R) to give the corresponding polysubstituted cyclopentenes **6** in moderate to good yields under the same conditions (Table 4, entries 11–18). Similarly, when the α-aryl ring had an electron-withdrawing group at the *para* position, good (75–88%) yields of **6** could be obtained (entries 12, 13, and 15), while lower (34–64%) yields were found with electron-donating substituents at the *para* position (entries 14, 16, and 17). The reaction also worked when R^2 was changed to an *n*-propyl group, and the yield of the cyclopentene **6** was 58% (entry 18). Alkyl acrylates (R^1 = H, R^2 = OR) could also serve as substrates to perform the cycloaddition reaction. The reactions proceeded smoothly to give **6** in similar (60–72%) yields, irrespective of the nature of the ester moiety (entries 19–23). This suggested that the steric size of the ester group in the acrylate had little influence on the reactivity.

The structures of all the reaction products were characterized by ^{1}H and ^{13}C NMR spectroscopy and HR-MS. The regioselectivity of the [3+2] cycloaddition reactions between the butatriene and aromatic aldehydes was confirmed by determination of the structure of **3e** by the X-ray crystallography (Figure 1). Similarly, the reaction regioselectivity between butatriene **1** and α,β-unsaturated carbonyl compounds could also be confirmed by the X-ray crystallographic analysis of compounds **6a** and **6c**. Hence, it was unambiguously confirmed that the regioselectivity of the [3+2] cycloaddition reactions between butatriene **1** and aromatic aldehydes **2** involved the attack of the α-position of butatriene to the aldehydic carbon of compounds **2**, followed by the ring closure between the aldehydic oxygen of compounds **2** with the γ-position of butatriene. On the other hand, the corresponding [3+2] cycloaddition reactions between butatriene **1** and α,β-unsaturated carbonyl compounds **5** involved the attack of the γ-position of butatriene to the β-position of **5**, followed by the ring closure between the α-position of compounds **5** and the α-position of butatriene.

Based on other similar phosphine-catalyzed [3+2] cycloaddition reactions,[2d,3g] a plausible reaction mechanism is proposed (Scheme 2). The reaction is believed to first involve a Michael-type addition reaction between PBu_3 to the β-position of butatriene **1** to generate a zwitterionic intermediate **A**. Subsequently, nucleophilic attack of the intermediate **A** to aldehydes **2** or the conjugated carbonyl compounds **5** give intermediates **B** or **D**, respectively. After proton transfer and elimination of PBu_3, the catalytic cycle is completed to give products **3** or **6** along with the regeneration of PBu_3.

We reasoned that the different regioselectivities exhibited in the cycloaddition reactions of aromatic aldehydes **2** and α,β-unsaturated carbonyl compounds **5** with butatriene **1** could be attributed to the difference in the steric environment of the substrates (Scheme 2). From the computational results of the stable conformation of the zwitterionic intermediate A (for computational details see the Supporting Information), it is noted that the plane defined by carbon atoms 5, 6 and 7 is nearly orthogonal to the one defined by carbon atoms 2, 3 and phosphorus atom (the dihedral angle is 90.6°). For the aromatic aldehydes **2**, the aldehydic carbon atom is sterically more hindered than the aldehydic oxygen atom. As a result, the preferred mode of regiochemistry would involve the attack of the α-position of the butatriene to the carbonyl carbon, followed by ring closure between the carbonyl oxygen and the γ-position of **1** to give the cycloaddition adduct **B**. On the other hand, for the α,β-unsaturated carbonyl substrates **5**, in order to



Scheme 2. Proposed reaction mechanisms.

avoid unfavorable steric repulsion in the transition state, the benzene ring of zwitterionic intermediate **A** and the substituents R^1 and R^2 in compounds **5** would be distant from each other during cycloaddition. As a result, γ-attack of the butatriene **1** to the β-position of compounds **5**, followed by ring closure between the α-atom of **5** and the α-position of **1** is the preferred mode of cyclization.

Conclusions

In summary, a series of polysubstituted 2,5-dihydrofurans and polysubstituted cyclopentenes with a quaternary carbon center were synthesized by using PBu_3-catalyzed [3+2]cycloaddition reactions involving butatriene derivative **1**. In both reactions the regioselectivity was dictated by the steric environment of the substrate molecules. For aromatic aldehydes **2** as the reaction partners, the polysubstituted 2,5-dihydrofurans **3** were formed by the α-attack of the butatriene **1** to the aldehydic carbon, followed by ring closure between the aldehydic oxygen and the γ-position of **1**. For α,β-unsaturated carbonyl compounds **5**, γ-attack of **1** to the β-position of **5**, followed by ring closure between the α-position of **5** and the α-position of **1** is the preferred mode of cyclization to give the polysubstituted cyclopentenes **6**. Further mechanistic investigations and studies on the synthesis of differently substituted butatrienes and the asymmetric [3+2]cycloaddition reaction are currently ongoing in our laboratory.

Experimental Section

General Information

PBu_3, $PPhMe_2$, PPh_2Me, PPh_3, and PMe_3 were purchased from Alfa Chemical Co. and were used as received. All re-

actions which required anhydrous conditions were run under argon atmospheres. Other commercially available reagents were used as received. THF was distilled from sodium benzophenone, while other solvents were dried by distillation over the appropriate drying reagents. Reactions were monitored by TLC on silica gel (GF-254) plates. Column chromatography was performed through silica gel (200–300 mesh). The petroleum ether (PE) used had a boiling range of 60–90 °C. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 MHz spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz) using tetramethylsilane or residual solvent signals as the internal reference ($CDCl_3$: $\delta_H = 7.26$, $\delta_C = 77.0$ ppm; acetone-d_6: $\delta_H = 2.04$, $\delta_C = 29.8$ ppm). Chemical shifts (δ) were reported in parts per million (ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz). Melting points were determined by use of a Reichert Microscope apparatus and are uncorrected. Single crystal X-ray diffraction measurements were made on a Bruker X8 APEX diffractometer working with graphite monochromated Mo-K_α radiation. Accurate mass measurements were obtained on a Bruker Daltonics APEX II 47e FT-ICR mass spectrometer or on a Fisons VG Autospec double focusing sector-field instrument.

CCDC 910662 (**3e**), CCDC 910664 (**6a**), and CCDC 910661 (**6c**) contain the supplementary crystallographic data for the paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Compounds 3

Aromatic aldehydes **2** (0.1 mmol) was added to a stirred solution of ethyl 5,5-diphenylpenta-2,3,4-trienoate **1** (28 mg, 0.1 mmol) in $CHCl_3$ (2 mL) under argon, followed by addition of PBu_3 (10 mg, 0.05 mmol). The reaction mixture was stirred at reflux for the given period of time. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, eluent: EtOAc/petroleum ether = 1/30) to yield compounds **3**.

Ethyl 5-(diphenylmethylene)-2-(4-nitrophenyl)-2,5-dihydrofuran-3-carboxylate (3a): Yellow solid; yield: 68%; mp 140–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.24 (d, $^3J_{H,H}$ = 8.8 Hz, 2H), 7.61 (d, $^3J_{H,H}$ = 8.8 Hz, 2H), 7.47–7.38 (m, 5H), 7.31–7.24 (m, 4H), 7.21–7.17 (m, 1H), 7.09 (d, $^3J_{H,H}$ = 2.0 Hz, 1H), 6.45 (d, $^3J_{H,H}$ = 1.6 Hz, 1H), 4.17–4.05 (m, 2H), 1.17 (t, $^3J_{H,H}$ = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.0 (C), 156.1 (C), 148.1 (C), 145.4 (C), 139.6 (C), 138.0 (C), 136.9 (C), 134.8 (CH), 131.0 (CH), 129.7 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 127.2 (CH), 123.7 (CH), 119.8 (C), 87.5 (CH), 61.1 (CH_2), 14.0 (CH_3); HR-MS (ESI): m/z = 428.1497, calcd. for $C_{26}H_{21}NO_5 + H^+$ [$M + H^+$]: 428.1492.

The spectroscopic data of compounds **3b–3m** can be found in the Supporting Information.

Synthesis of Ethyl 5-Benzhydryl-2-(4-nitrophenyl)-furan-3-carboxylate (4)

Aldehyde **2a** (15 mg, 0.1 mmol) was added to a stirred solution of ethyl 5,5-diphenylpenta-2,3,4-trienoate **1** (28 mg, 0.1 mmol) in CH_3CN (2 mL) under argon, followed by addition of PBu_3 (10 mg, 0.05 mmol). The reaction mixture was stirred at 60 °C for 2 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, eluent: EtOAc/petroleum ether = 1/20) to yield compound **4** as a brown solid; yield: 32 mg (74%); mp 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.23–8.15 (m, 4H), 7.36–7.30 (m, 4H), 7.28–7.25 (m, 2H), 7.23–7.21 (m, 4H), 6.43 (d, $^3J_{H,H}$ = 0.8 Hz, 1H), 5.52 (s, 1H), 4.30 (q, $^3J_{H,H}$ = 7.2 Hz, 2H), 1.32 (t, $^3J_{H,H}$ = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 163.2 (C), 157.4 (C), 153.7 (C), 147.5 (C), 140.6 (C), 135.5 (C), 128.70 (CH), 128.67 (CH), 127.2 (CH), 123.3 (CH), 117.3 (C), 112.3 (CH), 61.0 (CH_2), 50.7 (CH), 14.2 (CH_3), one tertiary carbon signal missing due to signal overlapping; HR-MS (ESI): m/z = 428.1497, calcd for $C_{26}H_{21}NO_5 + H^+$ [$M + H^+$]: 428.1492.

Synthesis of Compounds 6

β-Unsubstituted α,β-unsaturated esters and ketones **5**[8] (0.1 mmol) was added to a stirred solution of ethyl 5,5-diphenylpenta-2,3,4-trienoate **1** (28 mg, 0.1 mmol) in THF (2 mL) under argon, followed by addition of PBu_3 (10 mg, 0.05 mmol). The reaction mixture was stirred at reflux for the given period of time. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, eluent: EtOAc/petroleum ether = 1/20) to yield compounds **6**.

2-Ethyl 1-methyl 4-(diphenylmethylene)-1-phenylcyclopent-2-ene-1,2-dicarboxylate (6a): White solid; yield: 72%; mp 133–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.35–7.28 (m, 10H), 7.24–7.16 (m, 6H), 4.11 (q, $^3J_{H,H}$ = 7.2 Hz, 2H), 3.78 (s, 3H), 3.73 (d, $^3J_{H,H}$ = 16.8 Hz, 1H), 3.28 (d, $^3J_{H,H}$ = 16.8 Hz, 1H), 1.15 (t, $^3J_{H,H}$ = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 174.3 (C), 164.5 (C), 143.7 (CH), 142.1 (C), 141.9 (C), 141.4 (C), 141.2 (C), 141.0 (C), 139.4 (C), 130.1 (CH), 129.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 126.8 (CH), 62.4 (C), 60.4 (CH_2), 52.5 (CH_3), 48.3 (CH_2), 14.0 (CH_3); HR-MS (ESI): m/z = 439.1910, calcd. for $C_{29}H_{26}O_4 + H^+$ [$M + H^+$]: 439.1904.

The spectroscopic data of compounds **6b–6x** can be found in the Supporting Information.

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