Phosphine-Catalyzed Cycloaddition of 2,3-Butadienoates or 2-Butynoates with Electron-Deficient Olefins. A Novel [3 + 2] Annulation Approach to Cyclopentenes

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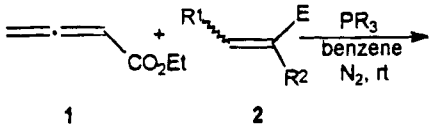
Efficient synthesis of the cyclopentane ring has been the target of a large number of methodological studies.[1,2] Among them, the [3 + 2] cycloaddition which has the advantage of multiple bond formation in a single operation is one of the focuses of intense synthetic efforts.[3-6] Many [3 + 2] cyclization reactions have been reported in literature,[3-6] but most of them suffered from the fact that the starting materials are not readily available. We report here a novel [3 + 2] annulation approach to cyclopentenes from electron-deficient olefins and simple 2,3-butadienoates or 2-butynoates as the three-carbon moiety under the catalysis of a phosphine.

Stirring a mixture of ethyl 2,3-butadienoate (**1**, 1 mmol) and ethyl acrylate (**2a**, 10 mmol) in dry benzene with 10 mol % of triphenylphosphine at rt gave **3a** as the major product together with a small amount of **4a** (yield 76%, **3a**/**4a** = 75:25). When tributylphosphine replaced triphenylphosphine as the catalyst, the reaction took place more rapidly, but gave **3a** and **4a** in slightly lower yield (66%, **3a**/**4a** = 75:25). A small amount of dimerization product of **2a** was also isolated.[7] No reaction occurred when triethylamine was used instead of the phosphine (eq 1).



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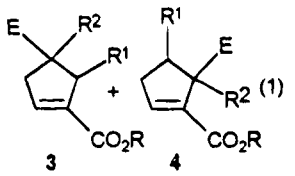
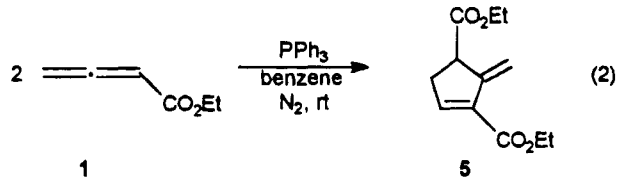


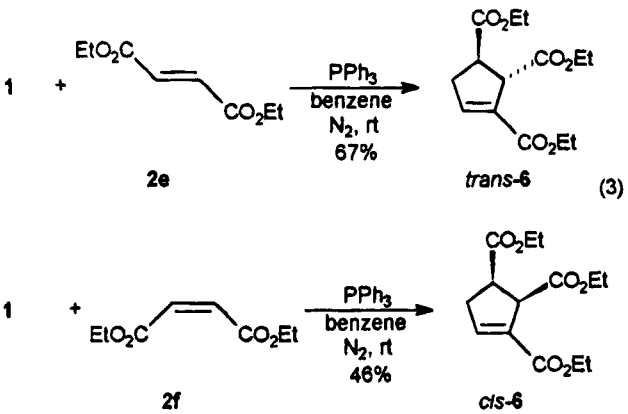
3 4 (1)

The structure of the olefin is crucial to the reaction. Electron-deficient olefins including ester, ketones, and nitrile reacted with **1** to give the cycloadducts in moderate to good yields (Table 1). For the reaction of **1** with 1-hexene, methyl (*E* or *Z*)-crotonate or methyl methacrylate, no expected product was isolated. Instead, we isolated a self-cycloaddition product of **1**, the structure of which was determined to be **5** (in 20% yield), together with a little amount of uncharacterized oligomers. A control experiment showed that stirring a benzene solution of **1** with 10 mol % of triphenylphosphine also afforded **5** in 20% yield and the same uncharacterized oligomers. It implies that **1** is more active as a trapping olefin than 1-hexene, methyl crotonate, and methyl methacrylate (eq 2).



1 5 (2)

Diethyl fumarate (**2e**) and diethyl maleate (**2f**)[8] reacted with **1** to yield the single product *trans*-**6** and *cis*-**6**,[9] respectively, implying that the stereochemistry remained unchanged in the cycloaddition reaction (eq 3).



A proposed mechanism of the reaction is outlined in Scheme 1. Phosphine first reacts with the allene **1** to form **7** or **8**, and then a [3 + 2] cycloaddition reaction occurs between the allylic carbanion and the electron-deficient olefin to form the cyclic intermediate **9A** and **9B** which are in equilibrium with **10A** and **10B**, respectively. Finally, the reaction gives products **3** and **4** with the regeneration of phosphine. Here, phosphine acts as a nucleophilic trigger.[10]

A 2,3-dienoate has been hypothesized to be an intermediate in the phosphine-catalyzed isomerization of

(1) For a recent review of five-membered ring syntheses, see: Hudlicky, T.; Price, J. D. *Chem. Rev.* **1989**, *89*, 1467.

(2) Trost, B. M.; Seoane, P.; Mignani, S.; Acemoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487 and references cited therein.

(3) For a recent review on [3 + 2] cycloaddition to five-membered carbocycles, see: Krohn, K. *Nachr. Chem. Tech. Lab.* **1987**, *35*, 700. Nakamura, E. In *Organic Syntheses in Japan. Past, Present and Future*; Noyori, R., Ed.; Tokyo Kagaku Dozin: Tokyo, 1992; p 275.

(4) For anionic [3 + 2] cycloadditions, see: Kauffmann, T. *Top. Curr. Chem.* **1980**, *92*, 109 and references cited therein. Beak, P.; Burg, D. A. *J. Org. Chem.* **1989**, *54*, 1647 and references cited therein. Ghera, E.; Yechezkel, T.; Hassner, A. *J. Org. Chem.* **1993**, *58*, 6716.

(5) For transition metal-catalyzed [3 + 2] cycloadditions, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183. Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 3825. Also see ref 2.

(6) For [3 + 2] cycloadditions involving free radical intermediates, see: Romanelli, A. L.; Ruckle, R. E., Jr.; Miller, K. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300 and references cited therein.

(7) The structure of the dimer is CH_2=C(CH_2CH_2COOEt)(COOEt). For the dimerization of acrylate in the presence of an organophosphorus(III) catalyst, see: Myman, F. Brit. Patent 1100350, 1965; *Chem. Abstr.* **1968**, *69*, 10093w. Kitazume, S. *Japan Kokai* **1977**, *77*, 105, 115; *Chem. Abstr.* **1978**, *88*, 89131f. Nemec, J. W.; Wuchter, R. B. U. S. Patent 4,145,559, 1979; *Chem. Abstr.* **1979**, *91*, 4960q. Amri, H.; Rtambaud, M.; Villieras, J. *Tetrahedron Lett.* **1989**, *30*, 7381.

(8) Commercial diethyl maleate contains a small amount of diethyl fumarate. In our reaction, the diethyl maleate was purified by column chromatography before use.

(9) The stereochemistry of the adducts *trans*-**6** and *cis*-**6** was assigned on the basis of the coupling constants of ring hydrogen atoms in ^{1}H NMR by irradiation and was further confirmed by 2D-NOESY spectra. For cyclopentenes, $J_{(cis)}$ is usually larger than $J_{(trans)}$, see: Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969. Davies, H. M. L.; Clark, T. J.; Church, L. A. *Tetrahedron Lett.* **1989**, *30*, 5057 and references cited therein.

(10) Trost, B. M.; Li, C.-J. *J. Am. Chem. Soc.* **1994**, *116*, 3167 and references cited therein.

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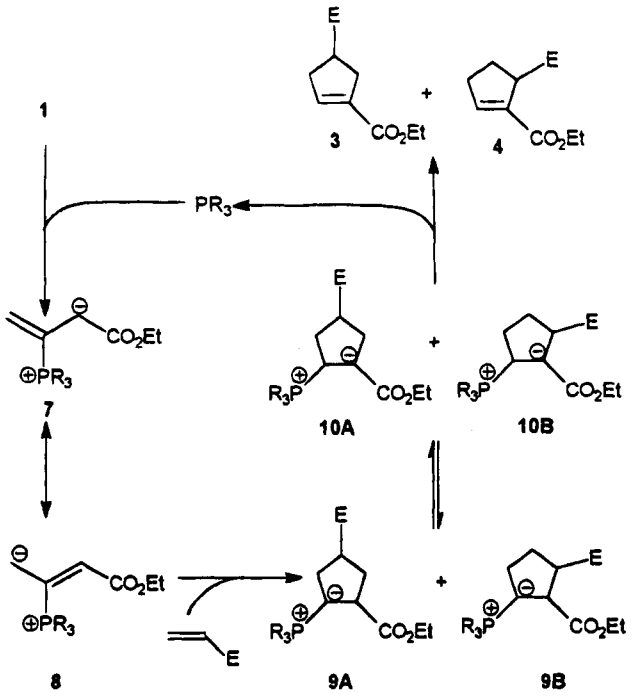
Table 1. Phosphine-Catalyzed Cycloaddition of 2,3-Butadienoates with Electron-Deficient Olefins

	olefin			products	
entry	2	E	PR_3	yield (%)	3:4[a]
1	**2a**[b]	COOEt	PPh_3	76	75:25
2	**2a**	COOEt[c]	PBu_3	66	75:25
3	**2b**[b]	COOMe	PPh_3	81	80:20
4	**2b**	COOMe[c]	PBu_3	66	85:15
5	**2c**[b]	COMe	PPh_3	55	63:37
6	**2d**[b]	CN	PPh_3	79	83:17[d]

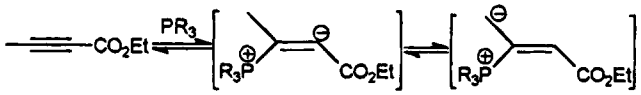
[a] Ratios were determined by isolation. [b] $R^1 = R^2 = H$. [c] 2 equiv of olefin was used. [d] Ratio was determined by ^1H NMR spectra.

Scheme 1



E = Electron withdrawing group

ynoates to 2,4-dienoates.[11,12] Is it possible to generate the intermediate **8** in situ from ethyl 2-butynoate (**11a**) (eq 4)? Should it be possible, the cycloaddition reaction



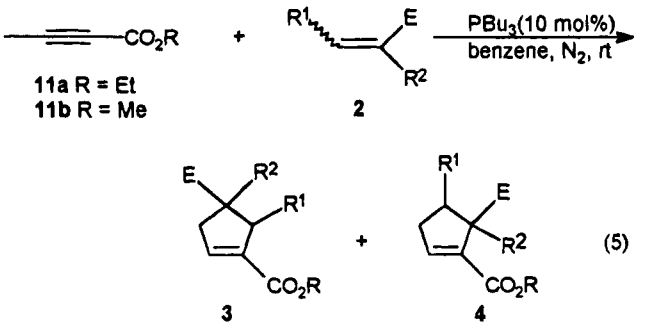
(4)

could occur using **11** as the starting material. Stirring a mixture of **11a** (1 mmol) and ethyl acrylate (**2a**, 2 mmol) with 10 mol % of tributylphosphine in benzene at rt under nitrogen did afford the same cycloadducts **3a** and **4a** in 85% isolated yield (**3a/4a** = 89:11) (eq 5). When triphenylphosphine was used as the catalyst, and the reaction was heated at 135 °C for a long time (24 h), only a trace of **3a** and **4a** were formed.[13] As shown in Table 2, **11** reacted with electron-deficient olefins normally to give the cycloadducts. The yields and regioselectivities were higher than that of the reaction of **1**. While methyl

Table 2. Cycloaddition of 2-Butynoates with Electron-Deficient Olefins under the Catalysis of Tributylphosphine

			products	
entry	11	2	yield (%)	3:4[a]
1	**11a**	**2a**[b]	85	89:11 (**3a:4a**)
2	**11a**	**2b**[b]	78	84:16 (**3b:4b**)
3	**11a**	**2d**[b]	80	93:7 (**3d:4d**)[c]
4	**11a**	**2e**	88	***trans*-6**
5	**11a**	**2f**	91	***trans*-6**
6	**11b**	**2b**	62	87:13 (**3b′:4b′**)
7	**11b**	**2g**[d]	46	72:28 (**3g:4g**)

[a] Ratios were determined by isolation. [b] See Table 1. [c] Ratio was determined by ^1H NMR spectra. [d] **2g**: R^1 = H, R^2 = Me, E = CO_2Me.



(5)

vinyl ketone failed to give the normal products, it polymerized in the presence of tributylphosphine. Both diethyl fumarate and diethyl maleate gave *trans*-**6** as the sole product, possibly due to the rapid isomerization of diethyl maleate to diethyl fumarate in the presence of tributylphosphine.[14] Triethylamine could not catalyze the reaction either.

In summary, we discovered a novel phosphine-catalyzed [3 + 2] cycloaddition reaction of 2,3-butadienoates or 2-butynoates with electron-deficient olefins to form the cyclopentene derivatives. The reaction is unprecedented in that 2-butynoates were used as the three-carbon moiety in a [3 + 2] cycloaddition reaction. The easy availability of the starting materials, the simplicity of the procedure, the high yield, and stereoselectivity of the products should offer great promise for the synthesis of cyclopentanoid natural products. The investigation of the scope, the mechanism, and the synthetic applications of this new cyclopentenation process is in progress.

Experimental Section

Ethyl 2.3-butadienoate (1) was prepared by reported method.[15]

Reaction of Ethyl 2,3-Butadienoate with Electron-Deficient Olefins. A Typical Procedure for the Preparation of Diethyl 3-Cyclopentene-1,3-dicarboxylate (3a) and Diethyl 2-Cyclopentene-1,2-dicarboxylate (4a). A mixture of ethyl 2,3-butadienoate (**1**) (112 mg, 1.0 mmol), ethyl acrylate (**2a**) (1.0 g, 10.0 mmol), and triphenylphosphine (26 mg, 0.10 mmol) in dry benzene (5 mL) was stirred at room temperature for 5 h under nitrogen. The reaction mixture was concentrated in vacuo, and the residue was chromatographed on silica gel

(11) Trost, B. M.; Kazmaier, U. *J. Am. Chem. Soc.* **1992**, *114*, 7933.
(12) Guo, C.; Lu, X. *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1921.
(13) No reaction occurred when the reaction mixture was heated at lower than 130 °C with triphenylphosphine as the catalyst. If the mixture was heated to higher temperature, the dimerization of acrylate became severe.
(14) A control experiment showed that when diethyl maleate in benzene was stirred with 10 mol % of tributylphosphine at rt under nitrogen, the maleate was completely isomerized to fumarate in 30 min. While triphenylphosphine was used as the catalyst, no isomerization occurred after 24 h. For other examples of phosphine catalyzed cis–trans isomerization of olefins, see: Ganguly, S.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1991**, 639. Larpent, C.; Meignan, G. *Tetrahedron Lett.* **1993**, *34*, 4331.
(15) Paik, Y. H.; Dowd, P. *J. Org. Chem.* **1986**, *51*, 2910.

(petroleum ether/ethyl acetate, 12:1) to give **3a** (120 mg) and **4a** (40 mg). The overall yield was 76%.

Diethyl 3-cyclopentene-1,3-dicarboxylate (3a):[16] oil; IR (neat) 1735, 1720, 1635, 1370, 1340, 1250, 1195, 1100, 1030, and 735 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.69 (t, 1H, J = 2.5 Hz), 4.13–4.23 (m, 4H), 3.23 (td, 1H, J_1 = 7.3 Hz, J_2 = 9.2 Hz), 2.80–2.91 (m, 4H), 1.25–1.31 (m, 6H); MS *m/z* 213 (12), 212 (M^+, 1), 167 (45), 166 (100), 139 (63), 111 (42), 93 (86), 67 (32).

Diethyl 2-cyclopentene-1,2-dicarboxylate (4a): oil, IR (neat) 1730, 1720, 1630, 1260, 1180, 1100, 1035, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.95 (t, 1H, J = 2.2 Hz), 4.13–4.21 (m, 4H), 3.73–3.79 (m, 1H), 2.47–2.70 (m, 2H), 2.30–2.42 (m, 1H), 2.05–2.18 (m, 1H), 1.23–1.30 (m, 6H); MS *m/z* 213 (M^+ + 1, 18), 167 (46), 139 (97), 138 (100), 111 (47), 93 (28), 66 (40), 65 (31); HRMS calcd for $C_{11}H_{16}O_4$ 212.1049, found 212.1069.

The following compounds were prepared similarly.

Methyl ethyl 3-cyclopentene-1,3-dicarboxylate (3b): oil; IR (neat) 1730, 1710, 1635, 1435, 1250, 1200, 1095, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.70 (t, 1H, J = 2.4 Hz), 4.20 (q, 2H, J = 7.1 Hz), 3.71 (s, 3H), 3.19–3.27 (m, 1H), 2.80–2.92 (m, 4H), 1.29 (t, 3H, J = 7.1 Hz); MS *m/z* 199 (M^+ + 1, 32), 167 (9), 153 (61), 152 (100), 139 (19), 125 (49), 111 (20), 93 (92), 67 (19), 65 (33); HRMS calcd for $C_{10}H_{14}O_4$ 198.0893, found 198.0907.

Methyl ethyl 2-cyclopentene-1,2-dicarboxylate (4b): oil IR (neat) 1720, 1635, 1345, 1270, 1200, 1100, 1040, and 765 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz) δ 6.96 (t, 1H, J = 2.4 Hz), 4.20 (q, 2H, J = 7.1 Hz), 3.74–3.82 (m, 1H), 3.71 (s, 3H), 2.47–2.71 (m, 2H), 2.30–2.40 (m, 1H), 2.06–2.15 (m, 1H), 1.27 (t, 3H, J = 7.1 Hz); MS *m/z* 199 (M^+ + 1, 35), 167 (19), 153 (25), 152 (49), 149 (22), 139 (38), 125 (57), 124 (100), 111 (27), 93 (44), 67 (43); HRMS calcd for $C_{10}H_{14}O_4$ 198.0893, found 198.0886.

Ethyl 1-acetyl-3-cyclopentene-3-carboxylate (3c): oil; IR (neat) 1725, 1710, 1635, 1370, 1265, 1240, 1100, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.68 (t, 1H, J = 2.2 Hz), 4.18 (q, 2H, J = 7.1 Hz), 3.30–3.41 (m, 1H), 2.63–2.94 (m, 4H), 2.2 (s, 3H), 1.29 (t, 3H, J = 7.1 Hz); MS *m/z* 182 (M^+, 2), 167 (1), 140 (43), 139 (100), 137 (27), 136 (71), 111 (82), 67 (53); HRMS calcd for $C_{10}H_{14}O_3$ 182.0933, found 182.0926.

Ethyl 1-acetyl-2-cyclopentene-2-carboxylate (4c): oil; IR (neat) 1725, 1710, 1630, 1350, 1260, 1100, and 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.97 (t, 1H, J = 2.4 Hz), 4.18 (q, 2H, J = 7.1 Hz), 3.88–3.94 (m, 1H), 2.49–2.70 (m, 2H), 2.20–2.35 (m, 1H), 2.23 (s, 3H), 1.95–2.05 (m, 1H), 1.27 (t, 3H, J = 7.1 Hz); MS *m/z* 183 (M^+ + 1, 69), 182 (M^+, 5), 140 (49), 137 (100), 112 (24), 111 (29), 67 (50); HRMS calcd for $C_{10}H_{14}O_3$ 182.0933, found 182.0896.

Ethyl 1-cyano-3-cyclopentene-3-carboxylate and ethyl 1-cyano-2-cyclopentene-2-carboxylate (3d + 4d): oil; IR (neat) 2220, 1730, 1710, 1635, 1370, 1260, 1095, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ [6.99 (t, J = 3.0 Hz) (**4d**), 6.71 (t, J = 2.3 Hz) (**3d**), 1H], 4.20–4.25 (m, 2H), [3.81–3.88 (m) (**4d**), 3.20–3.30 (m) (**3d**), 1H], 2.35–3.08 (m, 4H), 1.27–1.33 (m, 3H); MS *m/z* 165 (M^+, 8), 138 (6), 120 (100), 110 (18), 93 (10), 65 (22); HRMS calcd for $C_9H_{11}NO_2$ 165.0789, found 165.0747.

Diethyl 2-*exo*-methylene-3-cyclopentene-1,3-dicarboxylate (5): oil; IR (neat) 1725, 1595, 1250, 1175, 1065, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.08 (t, 1H, J = 1.4 Hz), 5.89 (d, 1H, J = 2.3 Hz), 5.31 (s, 1H), 4.13–4.28 (m, 4H), 3.72–3.77 (m, 1H), 2.99 (dt, 1H, J_1 = 3.4 Hz, J_2 = 19.7 Hz), 2.74 (ddd, 1H, J_1 = 2.7 Hz, J_2 = 8.5 Hz, J_3 = 19.7 Hz), 1.26–1.34 (m, 6H); MS *m/z* 224 (M^+, 16), 179 (68), 178 (100), 150 (38), 123 (39), 106 (26), 105 (76), 79 (49), 77 (43); HRMS calcd for $C_{12}H_{16}O_4$ 224.1048, found 224.1068.

***trans*-Triethyl 3-cyclopentene-1,2,3-tricarboxylate (*trans*-6)**: oil; IR (neat) 1730, 1640, 1375, 1270, 1220, 1105, 1035, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.84 (m, 1H), 4.20 (m, 6H), 4.07–4.10 (m, 1H), 3.39 (m, 1H, J_1 = 5.8 Hz, J_2 = 6.2 Hz, J_3 = 8.6 Hz) (determined by irradiation), 2.90–2.95 (m, 1H), 2.83–2.87 (m, 1H), 1.28 (m, 9H); MS *m/z* 285 (M^+ + 1, 90), 239 (74), 238 (57), 211 (88), 210 (48), 192 (39), 165 (100), 110 (43), 93 (60), 65 (49); HRMS calcd for $C_{14}H_{20}O_6$ 284.1260, found 284.1259.

***cis*-Triethyl 3-cyclopentene-1,2,3-tricarboxylate (*cis*-6)**: oil; IR (neat) 1740, 1730, 1640, 1375, 1265, 1195, 1100, 1040, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.96 (m, 1H), 4.10–4.21 (m, 6H), 4.02 (dd, 1H, J_1 = 2.5 Hz, J_2 = 9.1 Hz), 3.49 (q, 1H, J = 9.1 Hz), 3.13 (ddt, 1H, J_1 = 2.2 Hz, J_2 = 9.1 Hz, J_3 = 18.4 Hz), 2.75 (ddd, 1H, J_1 = 3.0 Hz, J_2 = 9.1 Hz, J_3 = 18.4 Hz), 1.24–1.29 (m, 9H); MS *m/z* 284 (M^+, 1), 239 (42), 211 (75), 210 (90), 166 (40), 165 (100), 138 (83), 93 (89); HRMS calcd for $C_{14}H_{20}O_6$ 284.1260, found 284.1240.

Reaction of 2-Butynoates with Electron-Deficient Olefins. A Typical Procedure for the Preparation of Dimethyl 3-Cyclopentene-1,3-dicarboxylate (3b′) and Dimethyl 2-Cyclopentene-1,2-dicarboxylate (4b′). A mixture of methyl 2-butynoate (**11b**, 98 mg, 1.0 mmol), methyl acrylate (**2b**, 172 mg, 2.0 mmol), and tributylphosphine (20 mg, 0.10 mmol) in dry benzene (5 mL) was stirred at rt for 10 h under nitrogen. The reaction mixture was chromatographed on silica gel (petroleum ether/ethyl acetate, 12:1) to give **3b′** (100 mg) and 4b′ (15 mg). The overall yield was 62%.

Dimethyl 3-cyclopentene-1,3-dicarboxylate (3b′): oil; IR (neat) 1720, 1635, 1435, 1350, 1270, 1220, 1095, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.69 (t, 1H, J = 2.1 Hz), 3.72 (s, 3H), 3.68 (s, 3H), 3.32 (m, 1H), 2.80–2.92 (m, 4H); MS *m/z* 185 (M^+ + 1, 8), 184 (M^+, 1), 153 (32), 125 (48), 93 (100), 65 (36); HRMS calcd for $C_9H_{12}O_4$ 184.0735, found 184.0740.

Dimethyl 2-cyclopentene-1,2-dicarboxylate (4b′):[17] oil; IR (neat) 1735, 1720, 1630, 1435, 1195, 1175, 780, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.96 (t, 1H, J = 2.3 Hz), 3.74 (s, 3H), 3.71 (s, 3H), 3.71–3.70 (m, 1H), 2.45–2.65 (m, 2H), 2.25–2.45 (m, 1H), 2.08–2.25 (m, 1H); MS *m/z* 185 (M^+ + 1, 7), 153 (10), 149 (100), 124 (2), 112 (10), 98 (8), 57 (12).

The following compounds were prepared similarly.

Dimethyl 1-methyl-3-cyclopentene-1,3-dicarboxylate (3g): oil; IR (neat) 1730, 1640, 1440, 1270, 1250, 1090, and 725 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.66 (t, 1H, J = 1.5 Hz), 3.74 (s, 3H), 3.71 (s, 3H), 3.06–3.17 (m, 2H), 2.36–2.54 (m, 2H), 1.34 (s, 3H); MS *m/z* 199 (M^+ + 1, 7), 198 (M^+, 1), 167 (23), 166 (53), 139 (61), 107 (100), 79 (83), 77 (29); HRMS calcd for $C_{10}H_{14}O_4$ 198.0892, found 198.0891.

Dimethyl 1-methyl-2-cyclopentene-1,2-dicarboxylate (4g): oil; IR (neat) 1720, 1625, 1435, 1275, 1250, 1090, 1055, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.87 (t, 1H, J = 2.0 Hz), 3.73 (s, 3H), 3.69 (s, 3H), 2.54–2.60 (m, 2H), 2.28–2.38 (m, 1H), 1.90–1.98 (m, 1H), 1.43 (s, 3H); MS *m/z* 199 (M^+ + 1, 92), 167 (19), 139 (100), 107 (40), 79 (50), 77 (17); HRMS calcd for $C_{10}H_{14}O_4$ 198.0892, found 198.0902.

Acknowledgment. We thank the National Natural Science Foundation of China and Chinese Academy of Sciences for financial support.

Supplementary Material Available: ^1H NMR spectra for compounds **3b**, **3b′**, **3c**, **3d** + **4d**, **3g**, **4a**, **4b**, **4c**, **4g**, **5**, ***cis*-6**, and ***trans*-6** and 2D NOESY spectra of ***cis*-6** and ***trans*-6** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO950033A

(16) Stevens, H. C.; Rinehart, J. K.; Lavanish, J. M.; Trenta, G. M. *J. Org. Chem.* **1971**, *36*, 2780.

(17) Suemune, H.; Tanaka, M.; Obaishi, H.; Sakai, K. *Chem. Pharm. Bull.* **1988**, *36*, 15.