[3 + 2] Annulation of Allylidenetriphenylphosphorane with 1,2-Diacylethylenes and 1,2-Diacylacetylenes: A One-Step Synthesis of Tri- and Tetrasubstituted Cyclopentadienes and Fulvenes

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Allylidenetriphenylphosphoranes underwent [3 + 2] annulation with 1,2-diacylethylenes at room temperature to give cyclopentadienes **11**−**17** having various substituents except for (*Z*)-3-acetylacrolein (**18**) which gave cyclohexadiene **19** derived from [3 + 3] annulation as the sole annulation product. The resulting cyclopentadienes were mixtures of the corresponding double-bond isomers which arose through an equilibrium process from the initially formed 1,3-dienes **a** under the weakly basic reaction conditions. Similar reactions of the phosphoranes with 1,2-diacylacetylenes afforded substituted fulvenes **24**, **25**, and **28** directly without the attendant formation of the corresponding benzene derivatives which come from another possible [3 + 3] annulation. The observed high level of the preference for the [3 + 2] annulation is discussed on the basis of the semiempirical PM3 MO calculations. The calculations suggested that the course of the annulation may be kinetically controlled at the oxaphosphetane-forming step of the intramolecular Wittig reaction.

Introduction

Considerable attention has been focused on the synthesis of substituted cyclopentadienes, since they serve as a useful construction unit of fused ring systems via an inter- and intramolecular Diels−Alder reaction[1] in addition to their increasing usefulness as ligands of various transition metals.[2] Fulvenes are also known to undergo several types of inter- or intramolecular cycloadditions, including [6 + 2], [6 + 4], and [4 + 2] cyclizations,[3] which may provide powerful tools for the construction of various ring systems. However, the utility of these cyclizations is limited due to the general inaccessibility of the substituted cyclopentadienes and fulvenes. Alkylcyclopentadienes or fulvenes are readily derived from cyclopentadiene by base-catalyzed alkylation[1] or condensation with aldehydes and ketones.[4] Application of these approaches to substituted cyclopentadienes is usually unsuccessful and leads to the formation of regioisomeric mixtures, although this route is often used for the preparation of the 1,3-substituted derivatives with relatively hindered substituents.[5] Several interesting methods for the direct preparation of di-, tri-, or tetrasubstituted cyclopentadienes include acid-catalyzed cyclization of 1,4-pentadien-3-ol,[6] palladium-mediated cyclization of 1,5-hexadien-3-ol,[7] rearrangement of vinylcyclopropylidene,[8] and cycloaddition of α,β-unsaturated Fisher carbene complexes to alkyne or alkene.[9,10] On the other hand, there are few precedents for the preparation of substituted fulvenes in a regioselective manner.[4a,11]

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(1) For some leading references, see: (a) Fringuelli, F.; Taticchi, A. *Dienes in the Diels−Alder Reaction*; John Wiley & Sons, Inc.: New York, 1990. (b) Corey, E. J.; Ravindranathan, T.; Terashima, S. *J. Am. Chem. Soc.* **1971**, *93*, 4326−4327. (c) Breitholle, E. G.; Fallis, A. G. *J. Org. Chem.* **1978**, *43*, 1964−1968. (d) Landry, D. W. *Tetrahedron* **1983**, *39*, 2761−2768. (e) Gallacher, G.; Ng, A. S.; Attah-Poku, S. K.; Antczak, K.; Alward, S. J.; Kingston, J. F.; Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 1709−1716. (f) Stille, J. R.; Grubbs, R. H. *J. Org. Chem.* **1989**, *54*, 434−444. (g) Sternbach, D. D.; Ensinger, C. L. *J. Org. Chem.* **1990**, *55*, 2725−2736. (h) Lei, B.; Fallis, A. G. *J. Am. Chem. Soc.* **1990**, *112*, 4609−4610.

(2) For some leading reviews, see: (a) Slocum, D. W.; Ernst, C. R. *Adv. Organomet. Chem.* **1972**, *10*, 79−114. (b) Macomber, D. W.; Hart, W. P.; Rausch. M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1−55. (c) Haltermann, R. L. *Chem. Rev.* **1992**, *92*, 965−994. (d) Ewing, D. F. *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Sainsbury, M., Eds.; Elsevier Science Publishers: Amsterdam, 1992; Vol. 2A and B, Chapter 4c.

(3) (a) Rigby, J. H. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 626. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons, Inc.: New York, 1985; pp 178−181. (c) Wang, Y.; Mukherjee, D.; Birney, D.; Houk, K. N. *J. Org. Chem.* **1990**, *55*, 4504−4506. (d) Coe, J. W.; Vetelino, M. G.; Kemp, D. S. *Tetrahedron Lett.* **1994**, *35*, 6627−6630.

(4) (a) For an exellent review, see: Zeller, K.-P. *Pentafulvenes. In Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, 1985; Vol. 5/2C, pp 504−684. (b) Buchi, G.; Berthet, D.; Decorzant, R.; Grieder, A.; Hauser, A. *J. Org. Chem.* **1976**, *41*, 3208−3209. (c) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849−1853. (d) Jacobs, S. J.; Schulz, S. A.; Javin, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744−1753. (e) Erden, I.; Xu, F.-P.; Sadoun, A.; Smith, W.; Sheff, G.; Ossun. M. *J. Org. Chem.* **1995**, *60*, 813−820 and references cited therein.

(5) (a) Alder, K.; Ache, H.-J. *Chem. Ber.* **1962**, *95*, 503−510. (b) McLean, S.; Hayes, P. *Tetrahedron* **1965**, *21*, 2313−2327. (c) Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41−84. (d) Hafner, K.; Thiele, G. F.; Mink, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1191−1192. (e) Jutzi, P.; Dahlhaus, J. *Synthesis* **1993**, 684−686.

(6) (a) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1−5. (b) Wochner, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 69−77. (c) Stein, D.; Sitzmann, H. *J. Organomet. Chem.* **1991**, *402*, C1-C3. (d) Garner, C. M.; Prince, M. E. *Tetrahedron Lett.* **1994**, *35*, 2463−2464.

(7) Zair, T.; Santelli-Rouvier, C.; Santelli, M. *Tetrahedron* **1993**, *49*, 3313−3324.

(8) (a) Scattebol, L. *Chem. Ind.* **1962**, 2146−2147; *Tetrahedron* **1967**, *23*, 1107−1117. (b) Holm, K. H.; Scattebol, L. *Acta Chem. Scand. Ser. B* **1985**, *39*, 549−561. (d) Paquette, L. A.; Gugelchuk, M.; McLaughlin M. L. *J. Org. Chem.* **1987**, *52*, 4932−4940. (c) Baird, M. S.; Jefferies, I. *Tetrahedron Lett.* **1986**, *27*, 2493−2496.

(9) (a) Aumann, R.; Heinen, H.; Dartmann, M.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2343−2347. (b) Flynn, B. L.; Funke, F. J.; Silveira, C. C.; de Meijere, A. *Synlett* **1995**, 1007−1010. (c) Aumann, R.; Meyer, A. G.; Frohlich, R. *Organometallics* **1996**, *15*, 5018−5027.

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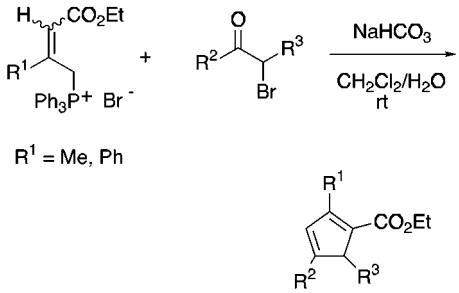
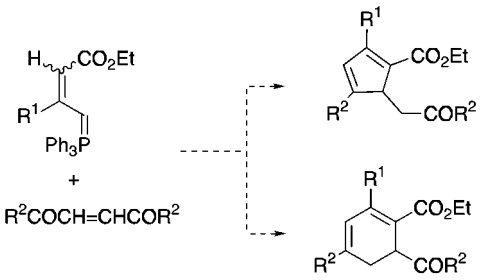
Scheme 1

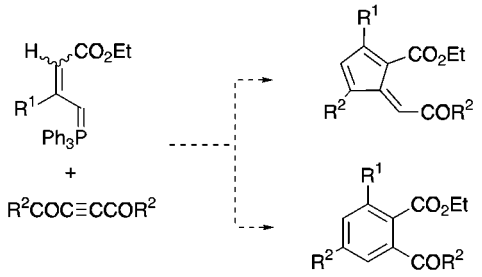


We recently demonstrated that allylidenetriphenylphosphorane undergoes a [3 + 2] annulation with α-halo ketones to give polysubstituted cyclopentadienes in a regioselective manner (Scheme 1).[12] The occurrence of this annulation reveals that allylidenephosphorane acts as a bifunctional reagent, first nucleophilic substitution at the γ-position of the phosphorane followed by an intramolecular Wittig reaction.[13] A similar [3 + 3] annulation of the phosphorane with α,β-unsaturated aldehydes and ketones has been reported to form cyclohexadienes in moderate yields.[14,15] In this context, we were interested in the reaction of allylidenetriphenylphosphorane with 1,2-diacylethylenes, in which there are two possible pathways for the annulation, leading to the formation of either cyclohexadiene or cyclopentadiene (Scheme 2). Although it was not clear which cyclization would complete effectively, we expected predominance for the [3 + 2] annulation because the cyclopentadiene formation with α-halo ketone proceeds more efficiently than the previous cyclohexadiene synthesis with α,β-unsaturated ketones. Similarly, 1,2-diacylacetylene could serve as a substrate for the annulation with the phosphorane (Scheme 3). However, phosphoranes including allylidenetriphenylphosphorane usually do not undergo Michael addition to acetylenes bearing electron-withdrawing groups and ylide interchange occurs via the phosphacyclobutene intermediate.[16] Accordingly, of particular interest is whether diacylacetylenes could take part as the Michael acceptor of allylidenephosphorane and furthermore whether a subsequent intramolecular Wittig reaction would prefer the [3 + 2] annulation to the [3 + 3] congener, in which the former would lead to fulvene formation with internal strain and the latter to the formation of stable benzenoids.

Scheme 2



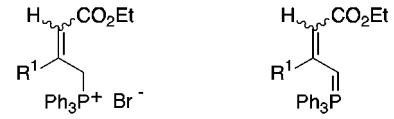
Scheme 3



Here, we report in detail that allylidenetriphenylphoshorane effects the [3 + 2] annulation with both 1,2-diacylacetylenes and 1,2-diacylethylenes and provides efficient methods for the regioselective preparation of the substituted cyclopentadienes and fulvenes in a one-step fashion.[17]

Results and Discussion

Cyclopentadiene Synthesis. Stabilized allylidenephosphoranes, (3-(ethoxycarbonyl)-2-substituted prop-2-enylidene)triphenylphosphoranes **4**−**6**, were used as starting phosphoranes. Since the phosphoranes can be generated in situ from the corresponding phosphonium salts in the presence of a weak base such as $NaHCO_3$, allylphosphonium salts **1**−**3**, in which **1** and **3** are in a



1 R^1 = Me
2 R^1 = Ph
3 R^1 = H

4 R^1 = Me
5 R^1 = Ph
6 R^1 = H

form of ca. 1:1 mixture of the *E*- and *Z*-isomers and **2** is a single *Z*-isomer,[12] were directly subjected to the reaction. When phosphonium bromide **1** was treated with dibenzoylethylene (**7**) in a heterogeneous medium of

(10) For other interesting cyclization, see: (a) Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466−469. (b) Sekiya, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5096−5100. (c) Koschinsky, R.; Kohli, T.-P.; Mayr, H. *Tetrahedron Lett.* **1988**, *29*, 5641−5644. (d) Lee, B. Y.; Moon, H.; Chung Y. K. *J. Am. Chem. Soc.* **1994**, *116*, 2163−2164. (e) Takahashi, T.; Xi, Z.; Kotora, M.; Xi, C. *Tetrahedron Lett.* **1996**, *37*, 7521−7524.

(11) (a) Lee, G. C. M.; Tobias, B.; Holmes, J. M.; Harcourt, D. A.; Garst, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9330−9336. (b) Silverberg, L. J.; Wu, G.; Rheingold, A. L.; Heck, R. F. *J. Organomet. Chem.* **1991**, *409*, 411−420.

(12) (a) Hatanaka, M.; Himeda, Y.; Ueda, I. *J. Chem. Soc., Perkin. Trans. 1* **1993**, 2269−2274. (b) Hatanaka, M.; Himeda, Y.; Imashiro, R.; Tanaka, Y.; Ueda, I. *J. Org. Chem.* **1994**, *59*, 111−119.

(13) (a) Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 583, 645, 830. (b) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1974**, *39*, 821−825. (c) Bestmann, H. J.; Roth, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 575−576.

(14) (a) Büchi, G.; Wüest, H. *Helv. Chim. Acta.* **1971**, *54*, 1767−1776. (b) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1973**, *106*, 3779−3787. (c) Dauben, W. G.; Ipaktschi, J. *J. Am. Chem. Soc.* **1973**, *95*, 5088−5089. (d) Dauben, W. G.; Hart, D. J.; Ipaktschi, J.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, 4425−4428. (e) Dauben, W. G.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, 3711−3714. (f) Neff, J. R.; Gruetzmacher, R. R.; Nordlander, J. E. *J. Org. Chem.* **1974**, *39*, 3814−3819. (g) Vedejs, E.; Bershas, J. P. *Tetrahedron Lett.* **1975**, 1359−1362. (h) Martin, S. F.; Desai, S. R. *J. Org. Chem.* **1977**, *42*, 1664−1666. (i) Hatanaka, M.; Yamamoto, Y.; Ishimaru, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1705−1706.

(15) For other annulations of allylidene(triphenyl)phosphorane, see: (a) Capuano, L.; Willmes, A. *Liebigs Ann. Chem.* **1982**, 80−86. (b) Capuano, L.; Triesch, T.; Willmes, A. *Chem. Ber.* **1983**, *116*, 3767−3773. (c) Ipaktschi, J.; Saadatmandi, A. *Liebigs Ann. Chem.* **1984**, 1989−1993. (d) Hatanaka, M.; Yamamoto, Y.; Ishimaru, T.; Takai, T. *Chem. Lett.* **1985**, 183−186.

(16) (a) Barluenga, J.; Lopez, F.; Sanchez-Ferrando, F. *Tetrahedron Lett.* **1988**, *29*, 381−384. (b) Johnson, A. W. *Ylides and Imines of Phosphorus*; John Wiley & Sons, Inc.: New York, 1993; pp 198−201. (c) Weiyu, D.; Zang, P.; Cao, W. *Tetrahedron Lett.* **1987**, *28*, 81−82. (d) Weiyu, D.; Weiguo, C.; Zhenrong, X.; Yuan, Y.; Zhijian, S.; Zhiheng, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 855−858.

(17) Preliminary report: Himeda, Y.; Hatanaka, M.; Ueda, I. *J. Chem. Soc., Chem. Commun.* **1995**, 449−450. Himeda, Y.; Ueda, I.; Hatanaka, M. *Chem. Lett.* **1996**, 71−72.

Scheme 4

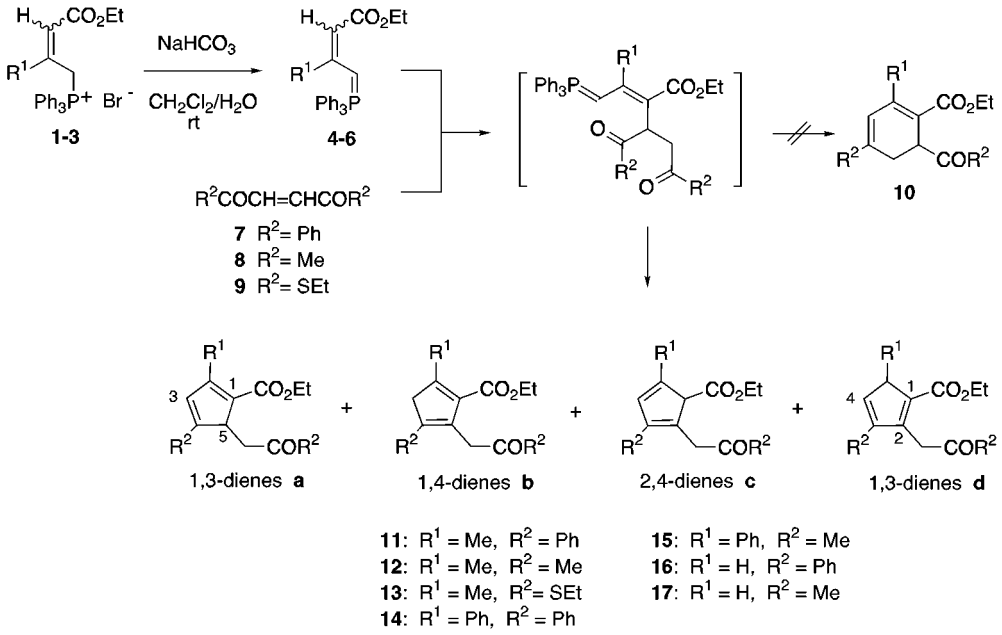
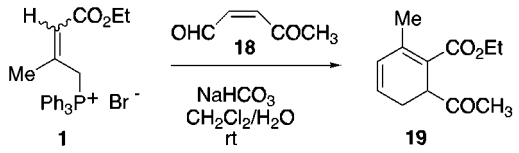


Table 1. Synthesis of Cyclopentadienes from Allyl(triphenyl)phosphonium Bromides and Diacylethylenes

			cyclopentadiene		
entry	phosphonium bromide (R^1)	diacylethylene (R^2)	no.	ratio of isomers[a] **a**:**b**:**c**:**d**	total yield[b]/%
1	**1** (Me)	**7** (Ph)	**11**	1:1:0:0	80
2	**1** (Me)	**8** (Me)	**12**	1:2:0:0	53
3	**1** (Me)	**9** (SEt)	**13**	1:1:0:0	32 (53[c])
4	**2** (Ph)	**7** (Ph)	**14**	3:9:1:0	90
5	**2** (Ph)	**8** (Me)	**15**	1:8:4:0	51
6	**3** (H)	**7** (Ph)	**16**	0:1:0:4	49
7	**3** (H)	**8** (Me)	**17**	**d** only	29

[a] The ratio of isomers was estimated on the basis of their NMR spectra. [b] Isolated yield. [c] The yield obtained under anhydrous conditions in THF in the presence of 1 equiv of NaHMDS.

dichloromethane and saturated aqueous $NaHCO_3$ at room temperature, the [3 + 2] annulation occurred nicely and cyclopentadiene was obtained in 80% yield as a 1:1 mixture of 1,3-diene **11a** and 1,4-diene **11b** without accompanying formation of the corresponding cyclohexadiene **10** (Scheme 4). The annulation is applicable to the preparation of various cyclopentadienes as illustrated in Table 1. When phosphonium bromide **1** was allowed to react with diacetylethylene (**8**) in a similar manner, a 1:2 mixture of 1,3-diene **12a** and 1,4-diene **12b** was obtained. Diethyl thiofumarate (**9**) afforded a 1:1 mixture of **13a** and **13b** in 53% yield when the reaction was carried out in THF using sodium hexamethydisilazide (NaHMDS) as a base; a lower yield in the heterogeneous medium is due to accompanying hydrolysis of **9**. 2-Phenylphosphonium bromide **2** also underwent annulation in the heterogenous medium to give the corresponding isomers along with alternate isomer 2,4-diene **c**. The reaction of **2** with **7** gave **14a**, **14b**, and **14c** in a ratio of 3:9:1 and that with **8** produced **15a**, **15b**, and **15c** in a ratio of 1:8:4 (entries 4 and 5). When phosphonium bromide **3** having no substituent at the 2-position was allowed to react with **7**, a 1:4 mixture of 1,4-diene **16b** and 1,3-diene **16d** was obtained. The reaction of **3** with **8** produced 1,3-diene **17d** as the sole observed isomer in 29% yield. On the other hand, [3 + 3] annulation occurred when unsymmetrical substrate **18** was allowed to react with **1**; cyclohexadiene **19** was obtained in 37% yield. It should arise from the initial Michael addition at the 3-position of **18** and subsequent internal Wittig reaction with the reactive aldehyde.

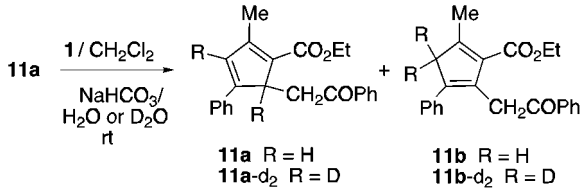


In order to determine the location of the double bonds in the resulting cyclopentadienes, we tried to isolate the isomers in a pure form. Although attempts to separate by means of column chromatography or HPLC were unsuccessful in all cases, 1,3-diene **11a** and 1,4-diene **14b** were fortunately isolated in pure form by crystallization from the corresponding isomeric mixtures. Compound **11a** was assigned as the 1,3-diene structure on the basis of the observation of a cross peak between the C-5 methine proton (δ 4.70) and the C-3 vinyl proton (δ 6.65) in the COSY ^{1}H NMR spectra. The accompanying isomer must be 1,4-diene **11b**, as indicated by an absorption (δ 3.50) due to the C-3 methylene protons. In agreement with this assignment, pure 1,4-diene **14b** showed two singlet peaks due to the C-3 methylene (δ 3.88) and the C-5′ methylene protons (δ 4.40) with the absence of any signals due to vinyl protons. Thus, the structure and the ratio of the 1,3-diene and the 1,4-diene produced in each case was estimated from ^{1}H NMR spectra of the crude product in comparison with those of **11a** and **14b**. The ^{1}H chemical shifts of the isomers are illustrated in Table 2. The generation of 2,4-dienes **c** (**14c** and **15c**) from the reactions of **2** with **7** and **8** was estimated from ^{1}H NMR spectra of each product mixture especially on the basis of observation of the cross peak between the C-1 methine (δ 4.88 for **14c**, δ 4.49 for **15c**) and the C-3 vinyl proton (δ 7.03 for **14c**, δ 6.73 for **15c**) in the COSY spectra. On the other hand, the location of the double bonds in 1,3-dienes **d** (**16d** and **17d**) was also determined in a similar manner on the basis of the ^{1}H NMR spectra.[18]

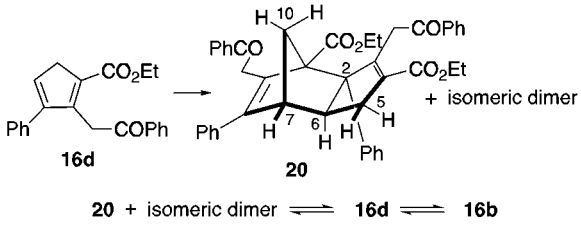
Table 2. ^{1}H Chemical shifts (δ) of the 1,3-Dienes 11a−15a and the 1,4-Dienes 11b−15b

1,3-diene **a**			1,4-diene **b**		
no.	3-H	5-H	no.	3-H	5′-methylene
11a	6.65	4.70	**11b**	3.50	4.35
12a	6.00	3.67	**12b**	3.02	3.58
13a	5.95	3.79	**13b**	3.25	3.95
14a	6.84	4.93	**14b**	3.88	4.40
15a	6.22	3.92	**15b**	3.41	3.61

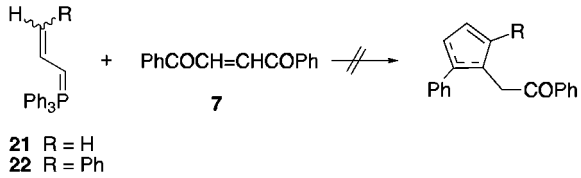
It is well-known that cyclopentadienes are usually unstable and readily undergo dimerization or 1,5-sigmatropic migration.[19] Those prepared above were stable for at least a week at room temperature, except for trisubstituted dienes **16d**, **16b**, and **17d** as described later. The formation of the double-bond isomers can be rationalized to come from either 1,5-sigmatropic migration or basic isomerization of the initial formed 1,3-dienes **a**. Isomerization of **11a** was examined in order to make it clear. Isomer **11a** was stable at room temperature for at least a week against 1,5-sigmatropic migration.[20] However, when **11a** was stirred in a heterogeneous medium of dichloromethane and saturated aqueous $NaHCO_3$ in the presence of a catalytic amount of **1** at room temperature, migration of the double bond occurred smoothly and led to the formation of a 1:1 equilibrium mixture of **11a** and **11b**. Deuterium-exchange experiment with a $NaHCO_3$−D_2O solution afforded a 1:1 mixture of 3,5-dideuteriated 1,3-diene **11a**-d_2 and 3,3-dideuteriated 1,4-diene **11b**-d_2. These findings indicate that the double-bond isomers arise through an equilibrium process from the initially formed 1,3-dienes **a** under the weakly basic reaction conditions via cyclopentadienyl anion formation.



The trisubstituted cyclopentadienes prepared from **3** showed somewhat different behavior from the tetrasubstituted derivatives. When the 4:1 mixture of **16d** and **16b** was left in a condensed state at room temperature for several hours, dimerization occurred to give a mixture of two isomeric dimers, of which the major isomer **20** was obtained as white powder while the minor one could not be purified because of its lability.[21] The structure of **20** was determined by a combination of COSY and NOESY spectra.[22] Evidence for the stereo- and regiochemical arrangement was mainly obtained from the NOESY spectra, which showed the cross peaks of the C-6 proton with the C-7 proton, the C-5α proton, and the C-2 phenyl protons. Interestingly, the dimerization is readily reversible. When a solution of dimer **20** in $CDCl_3$ was left at room temperature, ^{1}NMR spectra showed the partial liberation of monomers **16d** and **16b** within several hours and, after a week, almost complete formation of a 4:1



mixture of **16d** and **16b** with disappearance of the peaks due to the dimer. Evaporation of the $CDCl_3$ gave a mixture of the isomeric dimers again. However, the crude dimer was transformed into an unidentified polymeric substance upon further standing without solvent for a week. Trisubstituted cyclopentadiene **17d** did not dimerize under the same conditions, and when left at room temperature for a week, decomposed to a complex mixture from which no dimer was detected.



Attempted annulation of allylidenephosphorane **21** and the (3-phenylallylidene)phosphorane **22** with dibenzoylethylene (**7**) under various conditions failed to give any cyclopentadienes. The stronger basicity of the non- and semistabilized phosphoranes might trigger unfavorable side reactions, and hence the use of stabilized phosphorane such as **4**−**6** seems to be essential for the present annulation. Thus, these stabilized phosphoranes smoothly underwent annulation with 1,2-diacylethylenes as described above and provide a convenient method for the preparation of tri- and tetrasubstituted cyclopentadienes. The cyclopentadienes were obtained as mixtures of the double-bond isomers arising from the corresponding 1,3-dienes **a** via base-induced isomerization but not via 1,5-sigmatropic migration. Therefore, the product distribution may depend on the thermodynamic stability of the isomers. Dimerization was observed only for **16d**, although dimer **20** dissociated extremely readily to the monomer in a solution. The different behavior of **16d** and **17d** which did not effect the dimerization seems to be due to the electronic character of their C-3 substituents. Each isomer of the tetrasubstituted cyclopentadienes was stable against dimerization probably because of steric reasons.

Fulvene Synthesis. Taking advantage of the predominant formation of [3 + 2] annulation products with 1,2-diacylethylenes, we next investigated the reaction of the phosphoranes with 1,2-diacylacetylenes aiming at

(18) Compound **16d** showed the peak (δ 6.61) due to the C-4 vinyl proton and the peaks (δ 3.53) due to the C-5 methylene protons, and in addition the NOESY spectrum revealed the cross peak between the C-4 vinyl proton (δ 6.61) and the C-3 phenyl protons. The COSY spectrum of **17d** indicated the cross peaks between the C-5 methylene protons (δ 3.27) and the C-4 vinyl proton (δ 6.28) and between the former and the C-3 methyl protons (δ 1.92).

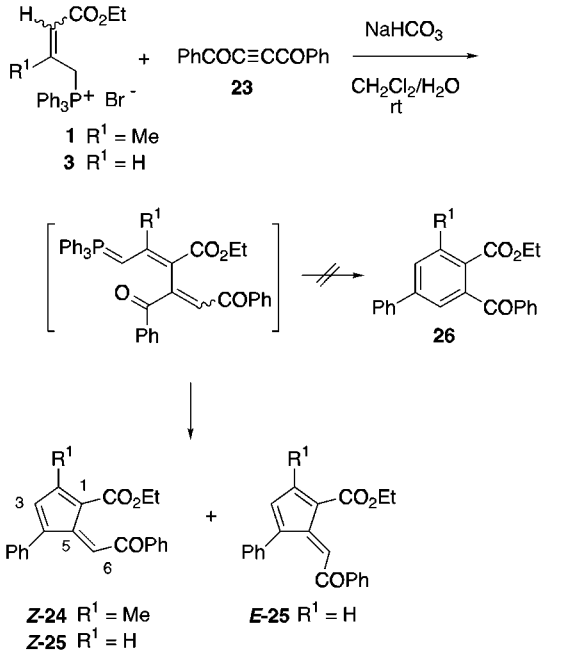
(19) (a) McLean, S.; Hayes, P. *Tetrahedron* **1965**, *21*, 2313−2327, 2329−2342, 2343−2351. (b) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187−217.

(20) The sigmatropic migration occurred when **11a** was heated in refluxing benzene for 3 h and led to the formation of a 2:1 mixture of **11a** and **11b**.

(21) It was suggested from observation of the following peaks in ^{1}H NMR spectra that the isomeric dimer might be the endo isomer of **20**: 3.40 (m, 1H, H-7), 2.86 (dd, J = 9.9, 18.0 Hz, 1H, H-5), 2.53 (bd, J = 18.0 Hz, 1H, H-5), 2.44 (dd, J = 1.8, 9.2 Hz, 1H, H-10), 2.01 (dd, J = 1.4, 9.2 Hz, 1H, H-10). However, a detailed examination was prevented by difficulty of purification and ready dissociation to the monomers in a solution.

(22) For dimerization of cyclopentadienylcarboxylate, see: (a) Franklin, E.; Mack, C. H.; Rowland, S. P. *J. Org. Chem.* **1968**, *33*, 626−632. (b) Minter, D. E.; Marchand, A. P.; Lu, S.-p. *Magn. Reson. Chem.* **1990**, *28*, 623−627.

Scheme 5



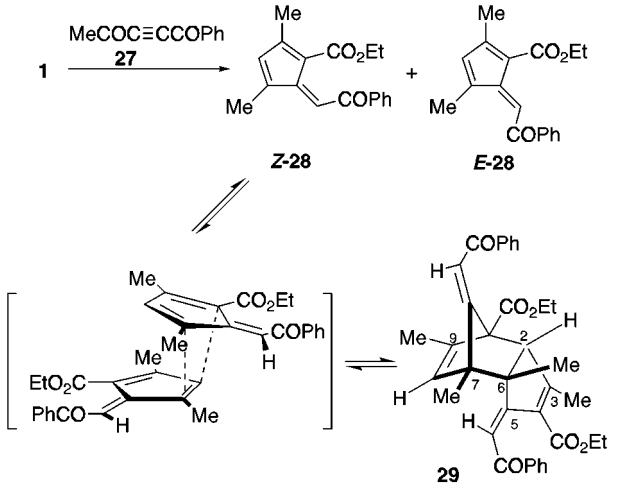
one-step synthesis of substituted fulvenes. Annulation of allylidenetriphenylphosphorane with alkynes attached to electron-withdrawing functionality has been reported only for the formation of substituted benzenes from allylidenephosphorane and perfluoro alkynoates.[16c,d] The annulation involves the first Michael addition at the α-position of the phosphorane and subsequent ylide interchange which is usually observed especially when the reaction of phosphorane with alkynes was carried out in aprotic solvents.[16b] We examined the reaction of allylidenephosphorane with 1,2-diacylethylenes in the heterogeneous medium described above to avoid the ylide interchange.

When phosphonium bromide **1** was allowed to react with dibenzoylacetylene (**23**) in the heterogeneous medium of dichloromethane and saturated aqueous $NaHCO_3$ at room temperature, fulvene ***Z*-24** was obtained as crystals in 88% yield (Scheme 5). The formation of the corresponding [3 + 3] annulation product **26** was not detected in the reaction mixture. Thus, Michael addition of the phosphorane occurred at the γ-position, and subsequent Wittig reaction favored the fulvene formation in a fashion analogous to the reaction with 1,2-diacylethylenes. Annulation of phosphonium salt **3** having no substituent at the C-2 position with **23** also gave the geometrical isomers ***Z*-25** and ***E*-25** in 38% and 28% yields, respectively. The ratio of *Z*- and *E*-isomers was not affected by the reaction temperature; a 3:1 mixture of ***Z*-25** and ***E*-25** was obtained in 25% yield when the reaction was carried out at 0 °C. It is however noted that the acetylene and 1,2-diacylethylenes are more efficient substrates than α-halo ketones, because **3** did not effect annulation with α-halo ketones but dimerization of the corresponding phosphorane **6**.[12a] The structure of ***Z*-24** was fully confirmed by a combination of the CH-COSY and long range CH-COSY spectra. The ^{13}C and ^{1}H chemical shifts of ***Z*-24** are given in Table 3. The geometry of the exocyclic double bond was assigned on the basis of the C-6 proton chemical shift. The exocyclic C-6 proton of ***E*-25** was observed at δ 8.34, while that of ***Z*-25** was centered at δ 7.08. It appears that the downfield shift observed for ***E*-25** is attributable to the

Table 3. ^{13}C and ^{1}H Chemical Shifts of *Z*-24

position	^{13}C chemical shift (ppm)	^{1}H chemical shift (ppm)
1	120.02	
2	157.01	
3	133.45	6.44
4	146.13	
5	143.96	
6	134.71	6.94

anisotropy of the ester carbonyl group.[3c,23] Similarly, the C-6 geometry of ***Z*-24** was determined to be *Z* on the basis of the C-6 proton chemical shift (δ 6.94).



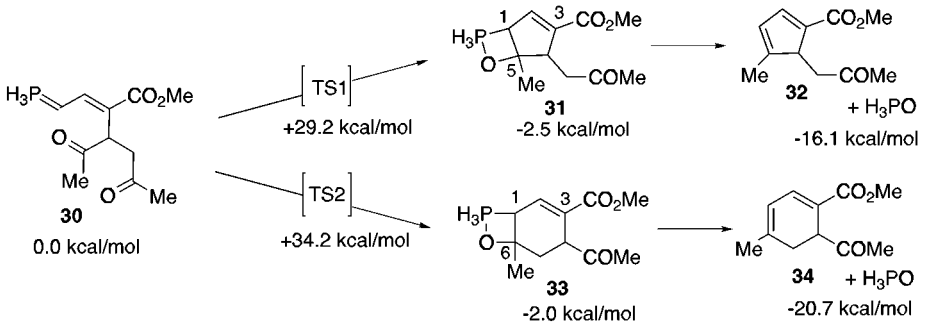
When the unsymmetrical substrate **27** was allowed to react with **1** in a similar manner, ***E*-28** and ***Z*-28** were isolated in 16% and 34% yields, respectively. No observation of the other regioisomers in the reaction mixture indicates that the initial Michael addition occurs regioselectively at the 3-position of **27**. Isomer ***Z*-28** was very unstable in the condensed state and was transformed easily into dimer **29**.[24] When a solution of **29** in $CDCl_3$ was left at room temperature overnight, ^{1}H NMR spectra showed partial dissociation of **29** into ***Z*-28**, implying reversibility of the dimerization. Structural confirmation of dimer **29** was accomplished by a combination of the COSY and NOESY spectra. Notable features of the NOESY spectra are the cross peaks between the C-2 proton and the C-3 methyl protons, between the C-5′ vinyl proton and the C-7 methyl protons, and between the C-3 methyl protons and the C-9 methyl protons. These facts strongly support the stereo- and regiochemical arrangement of structure **29**. In sharp contrast, isomer ***E*-28** was stable against dimerization after being left at room temperature for a week. This may suggest that approach of the two molecules of ***E*-28** is inhibited by the steric hindrance due to the *E*-oriented benzoyl group at the 6′-position. In addition, comparison of the behavior of ***Z*-28** with that of ***Z*-24** and ***Z*-25** indicates that the 4-phenyl substituent prevents the dimerization owing to steric bulk.

Thus, the annulation of 1,2-diacylacetylene with allylidenephosphorane provides efficient access to substituted fulvenes. The resulting 6-monoacylfulvenes, which

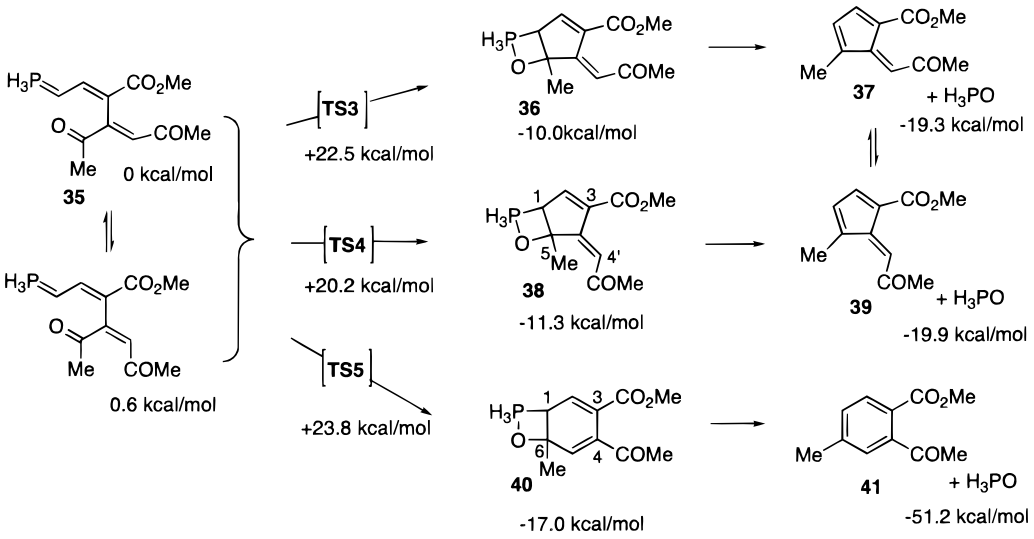
(23) The C-6 geometry was undoubtedly confirmed by the NOESY spectra; the cross peak between the C-6 proton and the C-4 methyl proton was observed for ***Z*-28** but not for ***E*-28**.

(24) For dimerization of fulvene, see: (a) Uebersax, B.; Neuenschwander, M.; Kellerhals, H.-P. *Helv. Chim. Acta* **1982**, *65*, 74−88. (b) Uebersax, B.; Neuenshwander, M.; Engel, P. *Helv. Chim. Acta* **1982**, *65*, 89−104.

Scheme 6



Scheme 7



are known only for a few examples,[4e,11b] were quite stable except for ***Z*-28** that dimerized readily. The distribution of *E*- and *Z*-isomers in each case seems to depend on the thermodynamic stability of the isomers, because isomerization of the 6-substituent can occur smoothly under the reaction conditions; ***E*-25** gave a 1:1 mixture of ***Z*-25** and ***E*-25** upon being stirred in saturated aqueous $NaHCO_3$ and dichloromethane in the presence of a catalytic amount of **3** at 30 °C for 12 h, while ***Z*-25** afforded a 2:1 mixture of ***Z*-25** and ***E*-25** under the same conditions.[25]

Calculations. Both annulations should proceed in a stepwise fashion as illustrated in Schemes 4 and 5. The C-3 carbanion of the 1,4-dipolar resonance form of allylidenephosphorane adds to 1,2-diacylethylene or 1,2-diacylacetylene, and subsequent intramolecular Wittig reactions provide cyclopentadiene or fulvene in a highly regioselective manner. The observed high level of [3 + 2] annulation is interesting, especially for a fulvene-forming reaction (Scheme 5) because an alternative [3 + 3] annulation would lead to the formation of much more stable benzene derivatives. We have carried out molecular orbital calculations on two model processes illustrated in Schemes 6 and 7 to clarify the origin of the high selectivity of the [3 + 2] annulation, especially for the fulvene-forming reaction. All calculations were carried out by the semiempirical PM3 method[26] with the Gaussian 92 package of programs;[27] the three Ph groups on P are replaced by H and other Ph and Et groups by Me in order to make the calculations practical. The PM3 method has previously been shown to be capable of successfully modeling a Wittig reaction.[28] The use of the rather simplified model is justified because we discuss only the relative stability of the transition states of the two competitive reaction routes for each compound (**30** and **35** in Schemes 6 and 7). Since the Wittig reactions proceed via the oxaphosphetane intermediates, two transition states, one for oxaphosphetane formation and the other for oxaphosphetane decomposition, may have to be considered for rationalizing the observed product selectivities. However, the extensive study by Vedejs revealed that oxaphosphetane reversal does not occur for a stabilized ylide and hence that product selectivity is determined in the oxaphosphetane formation step.[29] In the present calculations, therefore, only the oxaphosphetane-forming transition states were considered. Two ylides, **30** and **35**, five products (**32** and **34** for Scheme 6 and

(25) Significant deuterium incorporation at any position of the fulvene was not observed when the isomerization of ***E*-25** was carried out in D_2O solution. The isomerization also occurred at room temperature in an ether solution containing a weak base such as pyridine. It is likely that the extremely facile isomerization proceeds via an intermediary cyclopentadienyl anion produced by attack of a nucleophile at the 6-position.

(26) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220, 221−264.

(27) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andress, J. L.; Rachavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*, Gaussian Inc., Pittsburgh, PA, 1992.

(28) Mari, F.; Lahti, P. M.; McEwen, W. E. *Heteroatom Chem.* **1991**, *2*, 265−276. Mari, F.; Lahti, P. M.; McEwen, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 813−821.

(29) Vedejs, E.; Fleck, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 5861−5871. Vedejs, E. *Topics in Stereochemistry*: Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds; John Wiley & Sons, Inc.: New York, 1994; Vol. 21, pp 1−157.

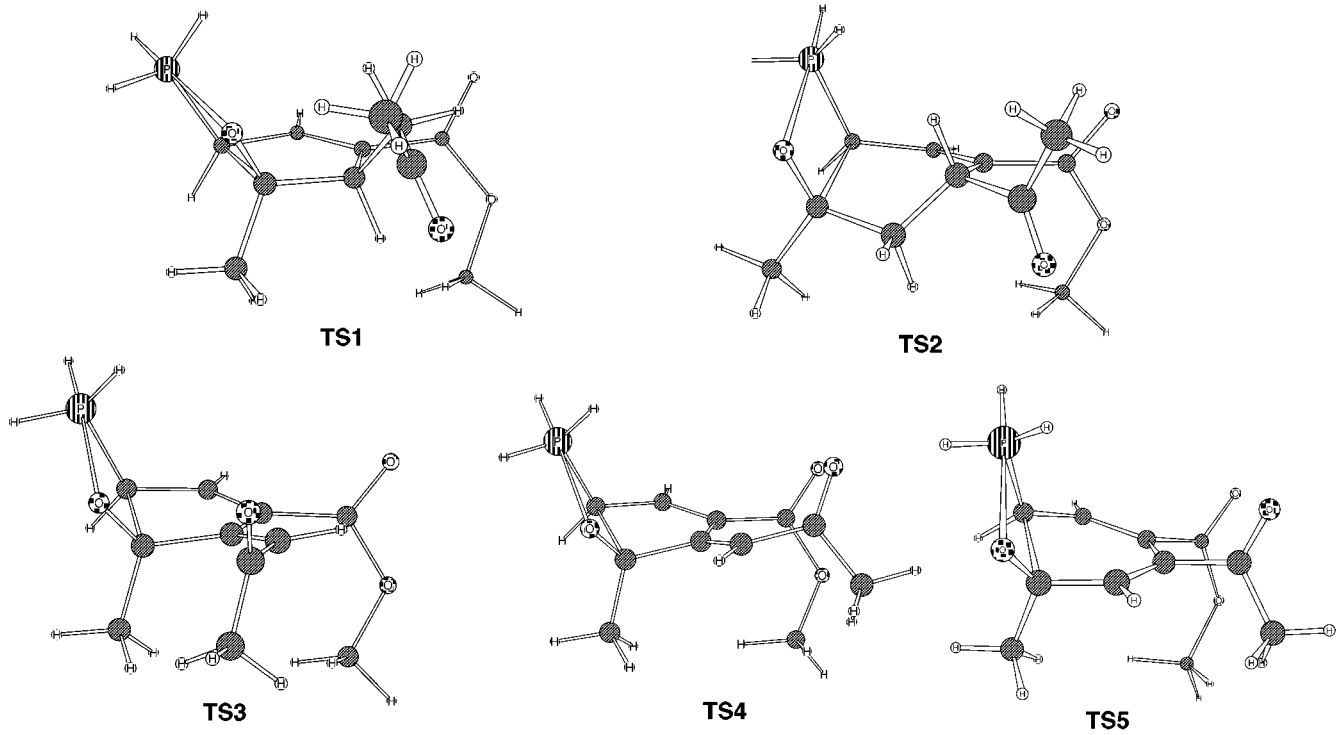


Figure 1. Optimized structures: transition states **TS1**, **TS2**, **TS3**, **TS4**, and **TS5** of oxaphosphetane-forming steps.

37, **39**, and **41** for Scheme 7), five oxaphosphetane intermediates, and five transition states leading to these intermediates were fully optimized. Several conformational isomers were examined for each species including the stereoisomeric pairs of **31**, **33**, **TS1**, and **TS2**, and only the most stable ones are considered here. The frequency calculations were carried out in order to confirm that the calculated structures are a local minimum or a transition state. Relative energies listed below include zero-point energy correction.

As summarized in Scheme 6, a pair of transition states for the oxaphosphetane formation (Figure 1) have much different energies; **TS2** which eventually gives cyclohexadiene is 5.0 kcal/mol higher in energy than **TS1** which leads to the cyclopentadiene derivative.[30] These give two oxaphosphetanes that have very similar stabilities. Thus, the calculations are consistent with the observed product selectivity. For the fulvene-forming reaction, two isomeric fulvenes, in addition to a six-membered product, were considered, and the results are summarized in Scheme 7. The two fulvene isomers were found to have similar stabilities, consistent with the fact that the reaction gave the mixture of the two isomers in all cases. Discussion of the subtle energy difference of the two isomers is probably not justified due to the limited accuracy of the semiempirical calculations. It should be noted, however, that the six-membered product **41** and the oxaphosphetane **40** leading to **41** have considerably lower energies compared to the corresponding five-membered species. Thus, the formation of the benzene derivative is thermodynamically favored over the fulvene derivatives. By contrast, the oxaphosphetane formation transition state in the benzene-forming pathway was found to be higher in energy than the transition states for the fulvene-forming pathways. Clearly observed exclusive fulvene formation is kinetically controlled in nature, which is fully consistent with the results reported by Vedejs.[29]

Since the benzene-forming pathway has a more stable oxaphosphetane and a less stable transition state than the fulvene-forming pathway, there should be some factor which makes the oxaphosphetane stable. A major origin may be an effective overlap of the two double bonds in oxaphosphetane **40**; the dihedral angle ($C_2-C_3-C_4-C_5$) in oxaphosphetane **40** is much smaller (1.8°) than that ($C_2-C_3-C_4-C_{4'}$, 7.6°) in oxaphosphetane **38**. It is noteworthy that the dihedral angle ($C_2-C_3-C_4-C_5$) in transition state **TS5** is larger (20.0°) than that ($C_2-C_3-C_4-C_{4'}$, 16.0°) in **TS4**, consistent with the relative stability of the two transition states.

Conclusion

The convenient syntheses of substituted cyclopentadienes and fulvenes were accomplished. In the [3 + 2] annulations, allylidenetriphenylphosporane acts as the 1,3-bifunctional unit having two nucleophic centers at the α- and γ-positions of the electron-delocalized structure. The utility of the phosphorane in annulation largely depends on which site effects nucleophilic addition. The alkylation occurs almost exclusively at the γ-position as demonstrated here and in the previous cyclopentadiene formation with α-halo ketone. This might be due to the steric hindrance at the α-position by the bulky triphenylphosphorus group. In addition, the present work demonstrated high regioselectivity of the subsequent intramolecular Wittig reaction for the 5-membered ring construction. The preference may be due to kinetic control as indicated by calculations.

Experimental Section

Melting points were obtained on a hot stage apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. ^{1}H NMR spectra were measured at 300

(30) The several conformational isomers were each examined for pairs of the stereoisomers of **TS1** and **TS2**, and the most stable transition states are depicted in Figure 1. The relative energies for the transition states and the oxaphosphetane stereoisomers that can be derived from those are listed in Scheme 6.

MHz in $CDCl_3$ on a Varian Gemini 300BB spectrometer, using $SiMe_4$ as the internal standard. ^{13}C NMR were recorded at 75 MHz on the spectrometer, and the solvent peak ($CDCl_3$, δ 77.0) was used for the internal standard. Mass spectra were recorded on a Hitachi M-80B spectrometer. Flash chromatography was performed on Wakogel C-300. The extracts were dried over $MgSO_4$ and evaporated under reduced pressure. CH_2Cl_2 was distilled from CaH_2. THF was distilled from sodium benzophenone ketyl.

Ethyl 2-Methyl-5-(2-oxo-2-phenylethyl)-4-phenyl-1,3-cyclopentadiene-1-carboxylate (11a) and 1,4-Diene Isomer (11b). Saturated aqueous $NaHCO_3$ (10 mL) was mixed with a solution of phosphonium bromide **1** (469 mg, 1.0 mmol) in dichlorometane (10 mL). To this well-stirred mixture was added a solution of 1,2-dibenzoylethylene (**7**, 236 mg, 1.0 mmol) in dichloromethane (2 mL), and the mixture was stirred at room temperature for 12 h under nitrogen. The aqueous layer was separated and extracted with dichloromethane. The combined organic layers were washed with water, dried, and then evaporated. The residue was passed through a short column of silica gel to remove triphenylphosphine oxide and further purified by flash chromatography with ethyl acetate/hexane (1:5) to afford a 1:1 mixture of **11a** and **11b** as an oil (277 mg, 80%): IR (neat) 1690, 1616, 1489, 1447, 1375 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (bd, J = 8.0 Hz, 2 × $^1/_2$H), 7.86 (bd, J = 8.0 Hz, 2 × $^1/_2$H), 7.56−7.23 (m, 8H), 6.65 (bs, 1 × $^1/_2$H), 4.70 (m, 1 × $^1/_2$H), 4.35 (s, 2 × $^1/_2$H), 4.11−3.97 (m, 2H), 3.50 (s, 2 × $^1/_2$H), 3.46 (dd, J = 6.1, 17.0 Hz, 1 × $^1/_2$H), 3.12 (dd, J = 3.5, 17.0 Hz, 1 × $^1/_2$H), 2.42 (s, 3 × $^1/_2$H), 2.41 (d, J = 1.4 Hz, 3 × $^1/_2$H), 1.08 (t, J = 7.1 Hz, 3 × $^1/_2$H), 1.07 (t, J = 7.1 Hz, 3 × $^1/_2$H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.04, 197.58, 164.79, 164.50, 156.26, 155.57, 155.28, 141.10, 137.00, 136.88, 136.42, 133.71, 133.31, 132.76, 132.69, 132.15, 131.38, 128.70, 128.38, 128.32, 128.28, 128.01, 127.97, 127.92, 127.77, 126.79, 126.69, 59.67, 59.35, 49.59, 47.27, 38.14, 38.04, 16.32, 15.64, 14.00, 13.90.

Trituration of the resulting oil in ethyl acetate−hexane gave pure crstals of **11a**: mp 115.5−117 °C; IR (Nujol) 1688, 1615, 1489, 1445, 1375 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, assignments were assisted by $^1H-^1H$ COSY experiments) δ 7.86 (bd, J = 8.0 Hz, 2H, ortho H of COPh), 7.53−7.23 (m, 8H, Ph), 6.65 (bs, 1H, 3-H), 4.70 (m, 1H, 5-H), 4.10−3.97 (m, 2H, OCH_2CH_3), 3.46 (dd, J = 6.1, 17.0 Hz, 1H, 5-CH_2), 3.12 (dd, J = 3.5, 17.0 Hz, 1H, 5-CH_2), 2.41 (d, J = 1.4 Hz, 3H, 2-CH_3), 1.08 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.62, 164.57, 156.27, 155.33, 136.99, 133.72, 132.68, 131.38, 128.69, 128.26, 128.00, 127.92, 126.79, 59.37, 47.25, 38.03, 15.62, 13.97; UV λ_{max} (MeOH) 330.5 (14 800), 235 nm (16 500). Anal. Calcd for $C_{23}H_{22}O_3$: H, 6.40; C, 79.74. Found: H, 6.33; C, 79.76.

Isomerization of 11a in D_2O. A solution of $NaHCO_3$ (0.5 g, 6.0 mmol) in D_2O (5 mL) was mixed with a solution of **11a** (98 mg, 0.283 mmol) in dichlorometane (10 mL). Phosphonium bromide **1** (40 mg, 0.085 mmol) was added to the well-stirred mixture, and the mixture was stirred at room temperature for 24 h under nitrogen. The aqueous layer was separated and extracted with dichloromethane. The combined organic layers were washed with water, dried, and evaporated. Purification by flash chromatography of the residue gave a 1:1 mixture of deuterated cyclopentadienes **11a**-d_2 and **11b**-d_2 as an oil (85 mg, 86%): IR (neat) 1690, 1599, 1489, 1447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (bd, J = 8.0 Hz, 2 × $^1/_2$H), 7.86 (bd, J = 8.0 Hz, 2 × $^1/_2$H), 7.56−7.23 (m, 8H), 4.35 (s, 2 × $^1/_2$H), 4.11−3.97 (m, 2H), 3.46 (d, J = 17.0 Hz, 1 × $^1/_2$H), 3.12 (d, J = 17.0 Hz, 1 × $^1/_2$H), 2.42 (s, 3 × $^1/_2$H), 2.41 (s, 3 × $^1/_2$H), 1.08 (t, J = 7.1 Hz, 3 × $^1/_2$H), 1.07 (t, J = 7.1 Hz, 3 × $^1/_2$H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.04, 197.58, 164.79, 164.50, 156.26, 155.57, 155.28, 141.10, 137.00, 136.88, 136.42, 133.71, 133.31, 132.76, 132.69, 132.15, 128.70, 128.38, 128.32, 128.28, 127.97, 127.92, 127.77, 126.79, 126.69, 59.67, 59.35, 38.14, 38.04, 16.32, 15.64, 14.00, 13.90; HRMS calcd for $C_{23}H_{20}D_2O_3$ 348.1693, found 348.1701.

Ethyl 2,4-dimethyl-5-(2-oxopropyl)-1,3-cyclopentadiene-1-carboxylate (12a) and 1,4-diene isomer (12b) were prepared from **1** and **8** according to the procedure described for the preparation of **11a** and **11b** to afford a 1:2 mixture of **12a** and **12b** as an oil: IR (neat) 1705, 1632, 1582, 1557, 1445, 1375 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.00 (d, J = 1.4 Hz, 1 × $^1/_3$H), 4.25−4.14 (m, 2H), 3.67 (bs, 1 × $^1/_3$H), 3.58 (s, 2 × 2/3H), 3.02 (s, 2 × 2/3H), 3.00 (dd, J = 16.6, 4.1 Hz, 1 × $^1/_3$H), 2.67 (dd, J = 16.6, 7.4 Hz, 1 × $^1/_3$H), 2.28 (s, 3H), 2.18 (s, 3 × 2/3H), 2.13 (s, 3 × $^1/_3$H), 1.94 (d, J = 1.4 Hz, 3 × $^1/_3$H), 1.88 (s, 3 × 2/3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.07, 206.92, 165.30, 164.66, 156.15, 155.53, 153.68, 136.91, 132.34, 131.47, 131.37, 130.07, 59.82, 59.42, 50.83, 42.47, 41.79, 30.30, 29.60, 16.32, 15.83, 15.35, 14.49, 14.44, 14.32, 13.14; HRMS calcd for $C_{13}H_{18}O_3$ 222.1255, found 222.1243.

Ethyl 4-(Ethylthio)-5-(2-(ethylthio)-2-oxoethyl)-2-methyl-1,3-cyclopentadiene-1-carboxylate (13a) and 1,4-Diene Isomer (13b). To a stirred suspension of phosphonium bromide **1** (469 mg, 1.0 mmol) in THF (20 mL) was added a 1 M sodium bis(trimethylsilyl)amide−THF solution (1.0 mL) at −30 °C under nitrogen, and the mixture was stirred for 1 h at 0 °C. The yellow suspension was cooled at −30 °C and treated with a solution of diethyl thiofumarate (**9**) (204 mg, 1.0 mmol) in THF (2 mL). The mixture was stirred at room temperature for 48 h and evaporated. The residue was chromatographed to give a 1:1 mixture of **13a** and **13b** as an oil (166 mg, 53%): IR (neat) 1692, 1609, 1497, 1375 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95 (s, 1 × $^1/_2$H), 4.27−4.16 (m, 2H), 3.95 (s, 2 × $^1/_2$H), 3.81−3.77 (m, 1 × $^1/_2$H), 3.25 (s, 2 × $^1/_2$H), 3.13 (dd, J = 15.4, 4.1 Hz, 1 × $^1/_2$H), 3.00 (dd, J = 15.4, 7.1 Hz, 1 × $^1/_2$H), 2.91−2.79 (m, 6 × $^1/_2$H), 2.73 (q, J = 7.4 Hz, 2 × $^1/_2$H), 2.35 (s, 3 × $^1/_2$H), 2.30 (d, J = 2.2 Hz, 3 × $^1/_2$H), 1.35 (t, J = 7.4 Hz, 3 × $^1/_2$H), 1.31 (t, J = 7.1 Hz, 3 × $^1/_2$H), 1.31 (t, J = 7.1 Hz, 3 × $^1/_2$H), 1.24 (t, J = 7.4 Hz, 3 × $^1/_2$H), 1.22 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.10, 196.37, 164.32, 164.05, 156.41, 155.99, 154.66, 138.17, 134.67, 131.87, 128.84, 128.09, 60.09, 59.41, 51.46, 50.06, 44.40, 43.10, 28.49, 26.75, 23.40, 23.25, 16.34, 15.70, 15.24, 14.68, 14.64, 14.43, 14.17, 13.51; HRMS calcd for $C_{15}H_{22}O_3S_2$ 314.1009, found 314.0991.

Ethyl 2,4-diphenyl-5-(2-oxo-2-phenylethyl)-1,3-cyclopentadiene-1-carboxylate (14a), 1,4-diene isomer (14b), and 2,4-diene isomer (14c) were prepared from **2** and **7** according to the procedure described for the preparation of **11a** and **11b** to afford a 3:9:1 mixture of **14a**, **14b**, and **14c** as an oil in 90% yield: IR (neat) 1692, 1597, 1493, 1447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (bd, J = 8.4 Hz, 2 × $^9/_{13}$H), 7.95 (bd, J = 8.4 Hz, 2 × $^1/_{13}$H), 7.88 (bd, J = 8.4 Hz, 2 × $^3/_{13}$H), 7.57−7.26 (m, 13H), 7.03 (d, J = 1.0 Hz, 1 × $^1/_{13}$H), 6.84 (d, J = 1.0 Hz, 1 × $^3/_{13}$H), 4.93 (m, 1 × $^3/_{13}$H), 4.88 (d, J = 1.0 Hz, 1 × $^1/_{13}$H), 4.40 (s, 2 × $^9/_{13}$H), 4.35−3.97 (m, 2H), 3.88 (s, 2 × $^9/_{13}$H), 3.59 (dd, J = 6.1, 16.8 Hz, 1 × $^3/_{13}$H), 3.25 (dd, J = 3.7, 16.8 Hz, 1 × $^3/_{13}$H), 1.03 (t, J = 7.1 Hz, 3 × $^1/_{13}$H), 0.98 (t, J = 7.1 Hz, 3 × $^9/_{13}$H), 0.97 (t, J = 7.1 Hz, 3 × $^3/_{13}$H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.77, 197.56, 197.47, 165.88, 164.10, 156.35, 155.29, 151.02, 143.52, 136.84, 136.19, 135.98, 133.89, 133.86, 133.02, 130.89, 130.75, 128.90, 128.67, 128.56, 128.44, 128.30, 128.18, 128.09, 127.98, 127.90, 127.84, 127.73, 127.69, 127.17, 126.99, 125.52, 60.35, 59.82, 48.53, 48.06, 38.39, 37.56, 13.81, 13.61; HRMS calcd for $C_{28}H_{24}O_3$ 408.1724, found 408.1691. Trituration of the resulting oil in ethyl ether−hexane gave pure crstals of **14b**: mp 110.8−112.0 °C ; IR (Nujol) 1705, 1692, 1597, 1493, 1446, 1373 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (bd, J = 8.4 Hz, 2H), 7.57−7.26 (m, 13H), 4.40 (s, 2H), 4.03 (q, J = 7.1 Hz, 2H), 3.88 (s, 2H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.78, 165.91, 151.03, 143.55, 136.91, 136.25, 136.05, 133.96, 133.03, 128.59, 128.22, 128.18, 128.02, 127.93, 127.76, 127.20, 60.37, 48.12, 37.59, 13.64; UV λ_{max} (MeOH) 324.0 (11 800), 243.5 nm (28 200). Anal. Calcd for $C_{28}H_{24}O_3$: H, 5.92; C, 82.33. Found: H, 5.83; C, 82.22.

Ethyl 4-methyl-5-(2-oxopropyl)-2-phenyl-1,3-cyclopentadiene-1-carboxylate (15a), 1,4-diene isomer (15b), and 2,4-diene isomer (15c) were prepared from **2** and **8** according to the procedure described for the preparation of **11a** and **11b** to afford a 1:8:4 mixture of **15a**, **15b**, and **15c** as an oil in 51% yield: IR (neat) 1715, 1631, 1601, 1559 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45−7.15 (m, 5H), 6.73 (d, J = 1.0 Hz, 1 × $^4/_{13}$H), 6.22 (bs, 1 × $^1/_{13}$H), 4.49 (bs, 1 × $^4/_{13}$H), 4.12 (q, J = 7.1 Hz, 2 × $^8/_{13}$H), 4.12−4.00 (m, 2 × $^5/_{13}$H), 3.92 (ddd, J = 7.3,

4.1, 1.1 Hz, 1 × $^{1}/_{13}$H), 3.61 (s, 2 × $^{8}/_{13}$H), 3.41 (s, 2 × $^{8}/_{13}$H), 3.11 (dd, J = 16.5, 4.1 Hz, 1 × $^{1}/_{13}$H), 2.77 (dd, J = 16.5, 7.3 Hz, 1 × $^{1}/_{13}$H), 2.22 (s, 3 × $^{8}/_{13}$H), 2.20 (s, 3 × $^{4}/_{13}$H), 1.99 (s, 3 × $^{8}/_{13}$H), 1.96 (d, J = 1.0 Hz, 3 × $^{4}/_{13}$H), 1.11 (t, J = 7.1 Hz, 3 × $^{1}/_{13}$H), 1.10 (t, J = 7.1 Hz, 3 × $^{4}/_{13}$H), 1.10 (t, J = 7.1 Hz, 3 × $^{8}/_{13}$H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.57, 205.85, 170.34, 166.26, 149.41, 144.51, 141.45, 139.94, 136.25, 134.56, 133.18, 132.10, 130.60, 128.64, 128.57, 128.06, 127.91, 127.66, 127.52, 127.14, 125.40, 61.18, 60.41, 60.18, 49.15, 41.90, 41.37, 29.70, 29.65, 14.09, 13.78, 13.47, 13.21; HRMS calcd for $C_{18}H_{20}O_3$ 284.1411, found 284.1405.

Ethyl 5-(2-oxo-2-phenylethyl)-4-phenyl-1,4-cyclopentadiene-1-carboxylate (16b) and ethyl 2-(2-oxo-2-phenylethyl)-3-phenyl-1,3-cyclopentadiene-1-carboxylate (16d) were prepared from **3** and **7** according to the procedure described for the preparation of **11a** and **11b** to afford a 1:4 mixture of **16b** and **16d** as an oil in 49% yield: ^{1}H NMR (300 MHz, $CDCl_3$, assignments were assisted by ^{1}H−^{1}H COSY and NOESY experiments) δ 8.03 (bd, J = 8.5 Hz, 2 × $^{1}/_{5}$H, ortho H of COPh), 7.95 (bd, J = 8.5 Hz, 2 × $^{4}/_{5}$H, ortho H of COPh), 7.54−7.25 (m, 8H, Ph), 7.39 (bs, 1 × $^{1}/_{5}$H, 2-H), 6.61 (bs, 1 × $^{4}/_{5}$H, 4-H), 4.52 (s, 2 × $^{4}/_{5}$H, 2-CH_2), 4.41 (s, 2 × $^{1}/_{5}$H, 5-CH_2), 4.13 (q, J = 7.1 Hz, 2 × $^{4}/_{5}$H, OCH_2CH$_3$), 4.11 (q, J = 7.1 Hz, 2 × $^{1}/_{5}$H, OCH_2CH$_3$), 3.53 (bs, 2 × $^{4}/_{5}$H, 5-H), 3.53 (bs, 2 × $^{1}/_{5}$H, 3-H), 1.15 (t, J = 7.1 Hz, 3 × $^{4}/_{5}$H, OCH$_2$CH_3), 1.14 (t, J = 7.1 Hz, 3 × $^{1}/_{5}$H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.02, 196.74, 164.49, 164.14, 151.30, 149.80, 145.56, 141.99, 139.42, 137.00, 135.67, 135.06, 133.91, 133.00, 132.91, 132.61, 128.51, 128.45, 128.31, 128.15, 128.06, 128.00, 127.55, 127.15, 60.17, 59.81, 43.81, 41.41, 38.13, 37.76, 14.22, 14.06; HRMS calcd for $C_{22}H_{20}O_3$ 332.1411, found 332.1436. The oil was converted into a dimeric mixture mainly containing **20** on leaving at room temperature overnight.

Ethyl 3-methyl-2-(2-oxopropyl)-1,3-cyclopentadiene-1-carboxylate (17d) was prepared from **3** and **8** according to the procedure described for the preparation of **11a** and **11b** to afford **17d** as an oil in 29% yield: IR (neat) 1698, 1628, 1557, 1444 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, assignments were assisted by ^{1}H−^{1}H COSY experiments) δ 6.28 (bs, 1H, 4-H), 4.21 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 4.00 (s, 2H, COCH_2), 3.27 (bs, 2H, 5-H), 2.23 (s, 3H, COCH_3), 1.92 (m, 3H, 3-CH_3), 1.31 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.24, 164.72, 152.40, 143.66, 133.09, 132.56, 59.78, 42.42, 40.84, 29.94, 14.42, 13.60; UV λ_{max} (MeOH) 285 nm (22 600); HRMS calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1091.

Ethyl 2-Methyl-6-(1-oxoethyl)-1,3-cyclohexadiene-1-carboxylate (19). Phosphonium bromide **1** (469 mg, 1.0 mmol) was allowed to react with 4-oxo-2-pentenal (**18**) (100 mg, 1.0 mmol) according to the procedure described for the preparation of **11a** and **11b**. Flash chromatography of the crude product gave **19** (76 mg, 37%) as an oil: IR (neat) 1711, 1574, 1400, 1356 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, assignments were assisted by ^{1}H−^{1}H COSY experiments) δ 6.04 (ddd, J = 9.4, 5.7, 2.9 Hz, 1H, 4-H), 5.91 (ddd, J = 9.4, 2.7, 0.9 Hz, 1H, 3-H), 4.24 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 3.59 (dd, J = 9.1, 3.5 Hz, 1H, 6-H), 2.76 (dddd, J = 18.0, 5.7, 3.5, 0.9 Hz, 1H, 5-H), 2.41 (dddd, J = 18.0, 9.1, 2.9, 2.7 Hz, 1H, 5-H), 2.25 (bs, 3H, 2-CH_3), 2.13 (s, 3H, COCH_3), 1.31 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, assignments were assisted by ^{13}C−^{1}H COSY, and long range ^{13}C−^{1}H COSY experiments) δ 209.13, 167.73, 145.11, 131.34 (4-*C*H), 130.62 (3-*C*H), 120.25, 60.37 (OCH_2CH$_3$), 46.44 (6-*C*H), 27.99 (CO*Me*), 25.77 (5-*C*H$_2$), 20.84 (2-Me), 14.25 (OCH$_2$CH_3); UV λ_{max} (MeOH) 286.5 nm (7000); HRMS calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1118.

Isolation of 1,4-Bis(ethoxycarbonyl)-3,9-bis(2-phenyl-2-oxoethyl)-2,8-diphenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene(20). The 1:4 mixture of **16b** and **16d** (276 mg, 0.83 mmol) in neat was heated at 40 °C for 30 min. The oil was taken into a 1:1 mixtue of ethyl ether and hexane (20 mL), and the solution was slowly condensed on a cold water bath until a white powder started to form. The powder was collected by filtration and washed several times with hexane to give **20** as white powder (20 mg, 8%). The filtrate contained mainly monomers **16b** and **16d** because of ready dissociation of **20** in the solution. **20**: IR (neat) 1736, 1688, 1597, 1447 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 0 °C, assignments were assisted by ^{1}H−^{1}H COSY and NOESY experiments) δ 7.92 (bd, J = 8.5 Hz, 2H, ortho H of COPh), 7.81 (bd, J = 8.5 Hz, 2H, ortho H of COPh), 7.56−7.20 (m, 16H, Ph), 4.30 (d, J = 17.7 Hz, 1H, CH_2COPh), 4.15−3.99 (m, 2H, OCH_2CH$_3$), 3.94−3.77 (m, 5H, OCH_2CH$_3$, CH_2COPh), 3.56 (bd, J = 9.6 Hz, 1H, 6-H), 3.25 (dd, J = 9.6, 17.5 Hz, 1H, 5-H$_\alpha$), 3.01 (s, 1H, H$_7$), 2.58 (dd, J = 3.4, 17.5 Hz, 1H, 5-H$_\beta$), 2.51 (d, J = 8.5 Hz, 1H, 10-H$_{anti}$), 2.36 (d, J = 8.5 Hz, 1H, 10-H$_{syn}$), 1.01 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), 0.98 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 0 °C) δ 198.16, 196.90, 172.08, 171.99, 148.51, 148.37, 137.54, 136.60, 136.55, 136.03, 133.78, 133.72, 133.03, 132.94, 128.56, 128.50, 128.37, 128.28, 127.90, 127.74, 127.39, 127.25, 127.16, 126.76, 67.20, 61.05, 60.78, 52.19, 47.85, 46.76, 42.01, 37.98, 37.84, 37.79, 13.78, 13.72; UV λ_{max} (MeOH) 244.0 nm (37 900). Anal. Calcd for $C_{44}H_{40}O_6$: H, 6.06; C, 79.49. Found: H, 6.05; C, 79.24.

(*Z*)-Ethyl 2-Methyl-5-(2-oxo-2-phenylethylene)-4-phenyl-1,3-cyclopentadiene-1-carboxylate (*Z*-24). Phosphonium bromide **1** (469 mg, 1.0 mmole) was allowed to react with **23** (234 mg, 1.0 mmole) according to the procedure described for the preparation of cyclopentadienes **11a** and **11b**. Purification by flash chromatography with ethyl acetate/hexane (1:5) of the crude product afforded ***Z*-24** (303 mg, 88%) as plates: mp 104.5−106.0 °C (ethyl acetate−hexane); IR (Nujol) 1715, 1663, 1595 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, assignments were assisted by ^{1}H−^{1}H COSY and NOESY experiments) δ 7.95 (bd, J = 8.5 Hz, 2H, ortho H of COPh), 7.57−7.36 (m, 8H, Ph), 6.94 (bs, 1H, =C*H*COPh), 6.44 (bs, 1H, 3-H), 3.84 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 2.37 (bs, 3H, 2-Me), 0.92 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.66, 164.25, 157.01, 146.13, 143.96, 136.78, 134.71, 133.95, 133.45, 133.37, 129.40, 129.02, 128.64, 128.18, 120.02, 59.78, 15.93, 13.73; UV λ_{max} (MeOH) 458.0 (2200), 424.0 (2400), 276.5 (22 000), 237.0 nm (26 000). Anal. Calcd for $C_{23}H_{20}O_3$: H, 5.85; C, 80.20. Found: H, 5.82; C, 80.14.

(*Z*)- and (*E*)-ethyl 5-(2-oxo-2-phenylethylene)-4-phenyl-1,3-cyclopentadiene-1-carboxylates (*Z*-25 and *E*-25) were prepared from **2** and **23** according to the procedure described for the preparation of ***Z*-24** to afford ***Z*-25** (38%) and ***E*-25** (28%). ***Z*-25:** oil; IR (neat) 1705, 1669, 1597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ assignments were assisted by ^{1}H−^{1}H COSY experiments) δ 7.94 (bd, J = 8.4 Hz, 2H, ortho H of COPh), 7.57−7.36 (m, 9H, Ph, 2-H), 7.08 (bs, 1H, =C*H*COPh), 6.58 (d, J = 2.6 Hz, 1H, 3-H), 3.91 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 1.00 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.67, 163.26, 145.67, 144.72, 143.39, 138.72, 136.66, 134.05, 133.39, 129.45, 129.01, 128.69, 128.63, 128.45, 128.27, 125.57, 60.08, 13.86; UV λ_{max} (MeOH) 458.0 (2600), 424.0 (2800), 243.0 nm (26 600); HRMS calcd for $C_{22}H_{18}O_3$ 330.1255, found 330.1238. ***E*-25:** oil; IR (neat) 1701, 1659, 1597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ assignments were assisted by ^{1}H−^{1}H COSY experiments) δ 8.34 (dd, J = 0.8, 1.2 Hz, 1H, =C*H*COPh), 7.57 (bd, J = 8.4 Hz, 2H, ortho H of COPh), 7.47 (dd, J = 0.8, 2.6 Hz, 1H, 2-H), 7.43 (bt, J = 7.4 Hz, 1H, para H of COPh), 7.27 (bt, J = 7.4 Hz, 2H, meta H of COPh), 7.10−6.90 (m, 5H, Ph), 6.43 (dd, J = 1.2, 2.6 Hz, 1H, 3-H), 4.33 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 1.39 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.42, 163.55, 144.63, 143,67, 143.05, 139.76, 136.87, 135.25, 133.23, 131.22, 128.97, 128.80, 128.11, 127.68, 127.52, 125.91, 60.11, 14.37; UV λ_{max} (MeOH) 458.0 (2400), 424.0 (2500), 242.5 nm (27 100); HRMS calcd for $C_{22}H_{18}O_3$ 330.1255, found 330.1229.

1-Phenyl-2-pentyne-1,4-dione (27). A solution of 1-phenyl-2-pentene-1,4-dione (730 mg, 4.2 mmol) in CCl_4 (30 mL) was treated with Br_2 (0.22 mL, 4.2 mmol), and the mixture was stirred at room temperature for 1 h and then evaporated. The residue was dissolved in acetone (30 mL) and treated with triethylamine (0.85 g, 8.4 mmol). After the mixture was refluxed for 1 h, the precipitated triethylammonium bromide was removed by filtration, and the filtrate was evaporated under reduced pressure. Flash chromatography with ethyl acetate/hexane (1:5) of the residue gave **27** (365 mg, 51%) as a pale yellow oil: IR (neat) 1694, 1651, 1597, 1451 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (bd, J = 8.4 Hz, 2H), 7.68 (tt, J = 7.4, 1.4 Hz, 1H), 7.53 (bt, J = 7.4 Hz, 2H), 2.52 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.86, 176.52, 135.59, 135.14, 129.69, 128.91, 86.69, 83.16, 32.56; HRMS calcd for $C_{11}H_8O_2$ 172.0524, found 172.0586.

(*Z*)- and (*E*)-ethyl 2,4-dimethyl-5-(2-oxo-2-phenylethylene)-1,3-cyclopentadiene-1-carboxylates (*Z*-28 and *E*-28) were prepared from **2** and **23** according to the procedure described for the preparation of ***Z*-24** to afford ***Z*-28** (34%) and ***E*-28** (16%), in which ***Z*-28** dimerized readily upon being left at room temperature after evaporation of the solvent and hence the physical data were taken as immediately as possible. ***Z*-28**: oil; IR (neat) 1669, 1599 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, assignments were assisted by ^{1}H−^{1}H COSY and NOESY experiments) δ 7.96 (bd, J = 8.4 Hz, 2H, ortho H of COPh), 7.58 (bt, J = 7.4 Hz, 1H, para H of COPh), 7.48 (bt, J = 7.4 Hz, 2H, meta H of COPh), 6.85 (bs, 1H, =C*H*COPh), 6.10 (q, J = 1.5 Hz, 1H, 3-H), 3.77 (q, J = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.26 (bs, 3H, 2-Me), 2.13 (d, J = 1.5 Hz, 3H, 4-Me), 0.90 (t, J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.82, 164.11, 158.43, 147.58, 139.75, 136.97, 133.30, 133.23, 129.36, 129.09, 128.64, 118.99, 59.55, 15.92, 13.78, 12.37; UV λ_{max} (MeOH) 459.0 (200), 377.0 (300), 273.5 (4600), 235.5 nm (3800); HRMS calcd for $C_{18}H_{18}O_3$ 282.1255, found 282.1266. ***E*-28**: mp 84.4−85.3 °C (ethyl ether−hexane); IR (Nujol) 1665, 1593 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ assignments were assisted by ^{1}H−^{1}H COSY and NOESY experiments) δ 8.13 (bs, 1H, =C*H*COPh), 8.02 (bd, J = 8.4 Hz, 2H, ortho H of COPh), 7.62 (bt, J = 7.4 Hz, 1H, para H of COPh), 7.49 (bt, J = 7.4 Hz, 2H, meta H of COPh), 6.05 (q, J = 1.5 Hz, 1H, 3-H), 4.30 (q, J = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.35 (bs, 3H, 2-Me), 1.84 (3H, d, J = 1.5 Hz, 4-Me), 1.37 (3H, t, J = 7.1 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.56, 164.59, 157.63, 146.29, 138.69, 136.52, 136.38, 135.44, 134.00, 129.27, 128.84, 118.96, 59.69, 16.77, 15.75, 14.49; UV λ_{max} (MeOH) 458.0 (600), 392.5 (900), 276.5 (13 200), 237.0 nm (11 900). Found: H, 6.41; C, 76.60; HRMS calcd for $C_{18}H_{18}O_3$ 282.1255, found 282.1285. Anal. Calcd for $C_{18}H_{18}O_3$: H, 6.43; C, 76.57.

(*5Z,10Z*)-5,10-Bis(benzoylmethylene)-1,4-bis(ethoxycarbonyl)-3,6,7,9-tetramethyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene (29). The Z-isomer ***Z*-28** dimerized within several hours to afford the dimer **29** quantitatively: oil; IR (neat) 1732, 1657, 1599 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ assignments were assisted by ^{1}H−^{1}H COSY and NOESY experiments) δ 7.96−7.90 (m, 4H, ortho H of COPh), 7.60−7.42 (m, 6H, Ph), 6.51 (s, 1H, 5-CH), 6.21 (s, 1H, 10-CH), 5.72 (q, J = 1.6 Hz, 1H, 8-H), 4.25−3.94 (m, 4H, OC*H*$_2$CH$_3$), 3.54 (bs, 1H, 2-H), 2.13 (s, 3H, 3-Me), 1.74 (d, J = 1.6 Hz, 3H, 9-Me), 1.46 (s, 3H, 7-Me), 1.36 (s, 3H, 6-Me), 1.11 (t, J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 1.01 (t, J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.79, 190.20, 169.98, 169.76, 165.54, 161.48, 159.76, 141.76, 138.55, 138.40, 137.55, 133.05, 132.46, 129.03, 128.64, 128.52, 128.45, 128.37, 113.43, 106.38, 64.38, 62.72, 60.87, 60.48, 56.82, 55.78, 22.08, 17.04, 15.54, 13.99, 13.83, 10.82; UV λ_{max} (MeOH) 316.0 (27 000), 258.5 nm (48 000); HRMS calcd for $C_{36}H_{36}O_6$ 564.2510, found 564.2504.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra (31 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.

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