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The First Synthesis of Phosphonoacrolein. Application to Diels−Alder Reaction as Heterodiene

Sadayuki Arimori, Ryoji Kouno, Tatsuo Okauchi, and Toru Minami*

Department of Applied Chemistry, Kyushu Institute of Technology, Sensui-cho, Tobata, Kitakyushu 804-8550, Japan

minami@che.kyutech.ac.jp

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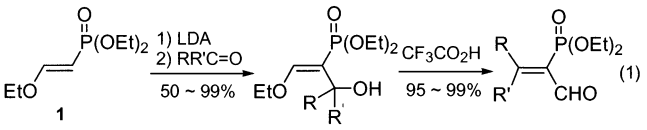
The first synthesis of phosphonoacrolein **3** was made in quantitative yield by acidic treatment of β-ethoxy-α-(methoxymethyl)vinylphosphonate **2**, derived from a β-ethoxy-α-phosphonovinyl anion and MOMCl. The phosphonoacrolein **3** easily underwent a hetero-Diels−Alder reaction with electron-rich alkenes **4a**−**f** or alkynes **9a**−**c** under mild conditions, and phosphono-substituted pyrans **5a**−**d**, **6e**,**f** or pyranopyrans **11a**−**c** were obtained in good to excellent yields. The reaction of **3** with cyclopentadiene and cyclohexadiene led to mixtures of [2 + 4] and [4 + 2] cycloadducts **7a**, **8a** and **7b**, **8b** in modest yields. The cycloaddition reaction between **3** and pyranopyran **13** or dibromocarbene and **13** resulted in [4 + 2] or [2 + 1] cycloadducts **14** or **15** in good yields.

Vinylphosphonates bearing various functional groups as well as other heteroatom-functionalized vinyl compounds (O, S, Se, Te, Si, Sn, etc. as heteroatom functionality) have been widely studied in organic synthesis during the last two decades.[1] We previously reported that vinylphosphonates bearing an electronegative group at the α-position underwent Lewis acid-catalyzed cyclizations,[2] for example, intramolecular ene reactions,[2a] [2 + 2] cycloadditions,[2b] and Nazarov cyclizations.[2c,d] Furthermore, we have recently shown that α-phosphonovinyl carbanions have interesting synthetic utility.[3] For instance, a convenient synthesis of a new type of β-substituted α-formylvinylphosphonates was achieved by utilizing the α-phosphonovinyl carbanions.[4] Its parent compound, β-unsubstituted α-formylvinylphosphonate, which we have named "phosphonoacrolein", is likewise expected to have potential synthetic utility as an intermediate reagent and industrial raw material, since phosphonoacrolein would be anticipated to show reactivities similar to those of not only its homologous β-substituted α-formylvinylphosphonates or analogous α-electronegative group-substituted vinylphosphonates but also acrolein. Synthesis and utilization of phosphonoacrolein are nevertheless left unexplored to date. Accordingly, we are interested in development of phosphonoacrolein and its synthetic applications. We now report the first synthesis of phosphonoacrolein and its application to hetero-Diels−Alder reactions.

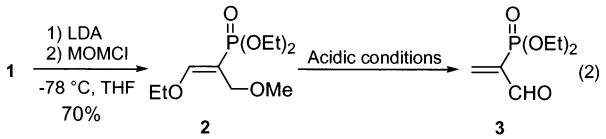
Results and Discussion

Synthesis of Phosphonoacrolein. We previously reported that β-substituted α-formylvinylphosphonates can be easily prepared in excellent yields by acid-catalyzed reaction of β-ethoxy-α-(hydroxymethyl)vinylphosphonates, which are derived from a β-ethoxy-α-phosphonovinyl carbanion and aldehydes or ketones (eq 1).[5]



(1)

Similar procedures are, however, inapplicable to the synthesis of phosphonoacrolein, since formaldehyde is difficult to use as an aldehyde. Instead, the reaction of the carbanion with chloromethyl methyl ether (MOMCl) produced a good yield of β-ethoxy-α-(methoxymethyl)-vinylphosphonate (**2**), followed by treatment with acids (e.g., CF_3COOH, Nafion NR-50, or AMBERLYST 15) to lead to the desired phosphonoacrolein **3** in quantitative yield (eq 2, entries 1−3 in Table 1).



(2)

* To whom correspondence should be addressed. Tel: +81-(0)93-884-3304. Fax: +81-(0)93-884-3300.

(1) For reviews on synthetic uses of vinylphosphonates, see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.

(2) (a) Minami, T.; Utsunomiya, T.; Nakamura, S.; Okubo, M. *J. Org. Chem.* **1994**, *59*, 6717. (b) Okauchi, T.; Kakiuchi, T.; Minami, T. *J. Org. Chem.* **1997**, *62*, 8419. (c) Minami, T.; Nakamura, M.; Fujimoto, K. *Chem. Comm.* **1992**, 190. (d) For a recent example of Nazarov cyclizations, see: Balczewski, P.; Mikolajczyk, M. *Org. Lett.* **2000**, *8*, 1153.

(3) For a review, see: Minami, T.; Okauchi, T.; Kouno, R. *Synthesis* **2001**, 349.

(4) For synthesis and synthetic application of α-phosphonovinyl carbanion, see: Minami, T.; Okauchi, T.; Matsuki, H.; Nakamura, M. *J. Org. Chem.* **1996**, *61*, 8132.

(5) For synthesis of α-formylvinylphosphonates via α-phosphonovinyl carbanion, see: Kouno, R.; Okauchi, T.; Minami, T. *J. Org. Chem.* **2000**, *65*, 4326.

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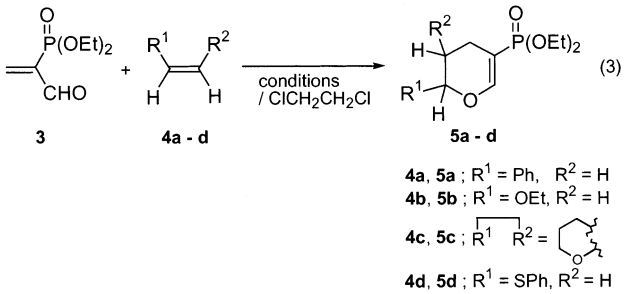
TABLE 1. Synthesis of Phosphonoacrolein (3)

entry	acid	solvent	time/h	yield[b]/%
1	CF_3CO_2H	CF_3CO_2H	3	quant
2	Nafion NR-50	CH_2Cl_2	24	99
3	AMBERLYST 15	CH_2Cl_2	12	99

[a] All reactions were carried out in the presence of H_2O (2.0 equiv) and excess of acid. [b] Isolated yield.

Synthetic Utilization of Phosphonoacrolein as a Hetero Diene. Reaction with Alkenes. To examine the reactivity of phosphonoacrolein **3** toward the carbon−carbon double bond, the reaction with styrene (**4a**), a simple olefin, was carried out under reflux in $ClCH_2CH_2Cl$[6] for 10 h to result in a hetero-Diels−Alder adduct,[7a,b] 3,4-dihydro-2-phenyl-5-phosphono-2*H*-pyran (**5a**), in 60% yield (eq 3, entry 1 in Table 2).



(3)

Similar treatment of **3** with electron-rich alkenes such as ethyl vinyl ether (**4b**), 3,4-dihydro-2*H*-pyran (**4c**), or phenyl vinyl sulfide (**4d**) led also to the corresponding 3,4-dihydro-5-phosphono-2*H*-pyrans **5b**−**d** in good to excellent yields (eq 3, entries 3−5 in Table 2). Cycloaddition between acrolein and vinyl ethers requires a long period of heating in an autoclave at 135−175 °C to produce 2-alkoxy-3,4-dihydro-2*H*-pyrans.[8] As shown above, phosphonoacrolein **3** is more reactive than its homologue, acrolein. The high reactivity may be rationalized by low π-LUMO energy of **3** compared to that of acrolein. [9]

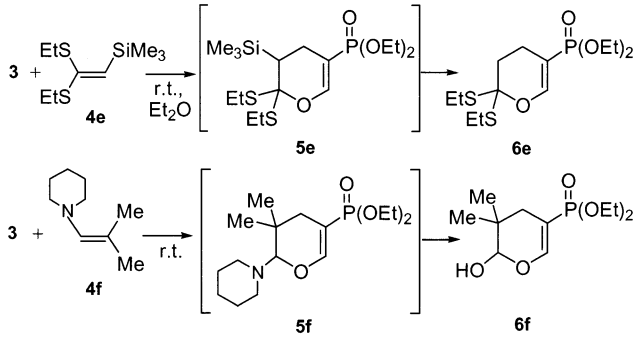
Addition of Lewis acid lowered the yield of products **5a** and **5d** due to the decomposition of acid-labile **3** (Table 2, entries 2 and 6). The similar [4 + 2] cycloaddition between **3** and silylketene dithioacetal **4e**[10] or enamine **4f**[11] successfully proceeded even at room temperature to produce dihydropyrans **6e**,**f** in 67−86% yields (Scheme 1, Table 2). The products **6e**,**f** were obtained via hydrolysis of initially formed [4 + 2] cycloadducts **5e**,**f** during workup. On the other hand, the cycloaddition of **3** with ethyl acrylate, an electron-deficient alkene, did not proceed (Table 2, entry 9). Thus, phosphonoacrolein (**3**) was found to act as a good heterodiene in the Diels−Alder reaction with various types of electron-rich alkenes.

TABLE 2. Intermolecular Hetero-Diels−Alder Reaction of 3 with Alkene[a]

entry	Alkene,	(4)	reaction condition: temp.	reaction condition: time/h	product[c] (yield/%)
1[b]	Ph	(**4a**)	reflux	10	**5a** (60)
2[b,d]		(**4a**)	reflux	11	**5a** (48)
3	EtO	(**4b**)	r.t.	3	**5b** (60)
4	O	(**4c**)	reflux	4	**5c** (92)
5	PhS	(**4d**)	reflux	3	**5d** (95)
6[d]		(**4d**)	reflux	6	**5d** (50)
7[e]	EtS, SiMe3, EtS	(**4e**)	r.t.	10	**6e** (86)
8	N, Me, Me	(**4f**)	r.t.	5	**6f** (67)
9	EtO_2C	(**4g**)	reflux	8	**5g** (-)

[a] Unless otherwise noted, the reactions were carried out in $ClCH_2CH_2Cl$ in the presence of 1.2 equiv of alkenes. [b] Excess (5 equiv) styrene was used. [c] Isolated yield. Yield is based on **3**. [d] This reaction was carried out in the presence of 1.3 equiv of $BF_3{\cdot}OEt_2$. [e] This reaction was carried out in Et_2O.

SCHEME 1



Reaction with Conjugated Dienes. We next explored whether **3** functions similarly to acrolein as both a 2π-component and a 4π-component in the Diels−Alder reaction with conjugated dienes.[12]

The reaction of **3** with 5 equiv of cyclopentadiene was carried out in toluene at 0 °C for 10 h. A mixture of two types of [4 + 2] adducts, 5-formyl-5-phosphonobicyclo-[2.2.1]hept −2-ene **7a** (29%) and 4-phsophono-2-oxabicyclo-[4.3.0]nona-3,8-diene **7b** (3%), was obtained in which **3** was added to the diene as 2π- and 4π-components, respectively. To examine temperature dependence on the

(6) Of the solvents ($ClCH_2CH_2Cl$, CH_2Cl_2, THF, toluene, and MeCN) screened, $ClCH_2CH_2Cl$ gave the best result.

(7) For a hetero-Diels−Alder reaction of alkenoylphosphonates with electron-rich olefins, see, for examples: (a) David, A, E.; Jefferey, S, J.; Edward, J, O. *J. Am. Chem. Soc.* **2000**, *122*, 1635. (b) Al-Badri, H.; Maddaluno, J.; Masson, S.; Collignon, N. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2255.

(8) For a hetero-Diels−Alder reaction of acrolein with ethyl vinyl ether, see, for example: Longley, R. I., Jr.; Emerson, W. S. *J. Am. Chem. Soc.* **1950**, *72*, 3079.

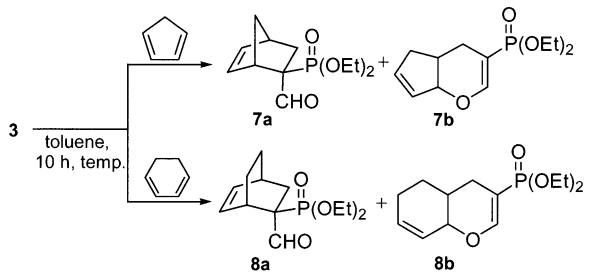
(9) The π-LUMO energies of acrolein and phosphonoacrolein are −0.188 and −0.452 (eV), which were calculated by MOPAC Ver. 6.1 (PM3).

(10) For synthesis and synthetic utilization of silylketene dithioacetal, see: Okauchi, T.; Tanaka, T.; Minami, T. *J. Org. Chem.* **2001**, *66*, 3924.

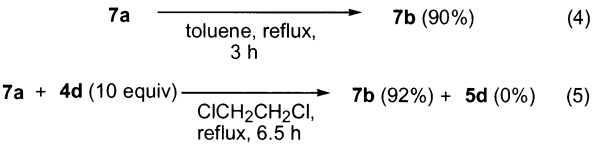
(11) For a hetero-Diels−Alder reaction of acrolein with enamines: Schut, R. N.; Liu, T. M. H. *J. Org. Chem.* **1965**, *30*, 2845.

(12) For a Diels−Alder reaction of acrolein with cyclohexadiene, see, for example: White, K. B.; Reusch, W. *Tetrahedron* **1978**, *34*, 2439.

SCHEME 2



products, similar treatment of **3** with the diene at room temperature or at reflux led to a mixture of **7a** (18%) and **7b** (39%) (Scheme 2, entries 1−3 in Table 3). A similar reaction occurred on treatment of **3** with cyclohexadiene at room temperature and at reflux to form a mixture of the corresponding [4 + 2] adducts **8a** and **8b** in 12−15% and 9−34% yields, respectively, while the reaction at 0 °C afforded none of adduct (Scheme 2, entries 4−6). The preferential formation of **7a**, **8a**, over **7b**, **8b**, at rather low temperatures (0 °C or room temperature) and of **7b**, **8b** over **7a**, **8a** at elevated temperature was observed. These results suggest that the cycloadducts **7a**, **8a** are kinetically controlled products and their isomers **7b**, **8b** are thermodynamically controlled ones, or **7a**, **8a** are converted into **7b**, **8b** by a hetero-Cope rearrangement.[13] To make this reaction mechanism clear, we attempted to transform **7a** into **7b** or **5d** by the following two methods. The isolated adduct **7a** was subjected to heat in toluene or in dichloroethane containing excess **4d** to produce exclusively **7b** in excellent yields in both cases (eqs 4 and 5), and the adduct **5d** derived from hetero Diels−Alder reaction of **3** with **4d** was not obtained at all (eq 5). Thus, the adducts **7b**, **8b** were produced via hetero-Cope rearrangement from **7a**, **8a**.[14] These results indicate that substrate **3** reacted with cyclopentadiene and cyclohexadiene as a 2π-component.



Reaction with Alkynes. We are furthermore interested in the reaction of **3** with alkynes. When a mixture of phenylacetylene (**9a**) (1.2 equiv) and **3** was subjected to similar reaction conditions ($ClCH_2CH_2Cl$, reflux), an anticipated 1:1 hetero-Diels−Alder adduct **10a** was not formed, but a 1:2 adduct, 4,4a,5-trihydro-8a-phenyl-3,6-diphosphonopyrano[3.2-*b*]pyran **11a**, was exclusively obtained in 67% yield (Scheme 3, entry 1 in Table 4).

This result indicates that **9a** reacted with **3** to give a [4 + 2] cycloadduct, 6-phenyl-4*H*-pyran **10a**, followed by the reaction with **3** to lead to **11a** at a faster rate than the reaction of starting **9a** with **3**. Use of ethynyl ethyl ether (**9b**) or methyl (trimethylsilyl)ethynyl sulfide (**9c**) instead of **9a** as substrates similarly led to the corresponding 1:2-adducts **11b**,**c** in 37−85% yields (Table 4, entries 2 and 3). Thus, the same type of 2:1-hetero Diels−Alder adducts between **3** and alkynes **9** were produced, regardless the substituents on **9** used.

Next, we examined the reactivity of **3** toward 4*H*-pyrano[3.2-b]pyran **13** containing the sterically hindered C=C bond at the fused position. As illustrated in Scheme 4, an aimed pyranopyran **13** was prepared in 81% overall by oxidation of the compound **11c** with *m*-chloroperbenzoic acid to sulfoxide **12** and subsequent thermal elimination.[15]

When the compound **13** was treated with 3 equiv of **3** at reflux in toluene for 17 h, a hoped-for hetero-Diels−

TABLE 3. Intermolecular Diels−Alder Reaction of 3 with Cyclopentadiene or Cyclohexadiene[a]

entry	Diene	temp.	product[b] (yield/%)	
1		0 °C	**7a** (29)	**7b** (3)
2		r.t.	(18)	(4)
3		reflux	(-)	(39)
4		0 °C	**8a** (-)	**8b** (-)
5		r.t.	(12)	(9)
6		reflux	(15)	(34)

[a] All reactions were carried out in the presence of 5.0 equiv of dienes for 10 h in toluene. [b] Isolated yield.

SCHEME 3

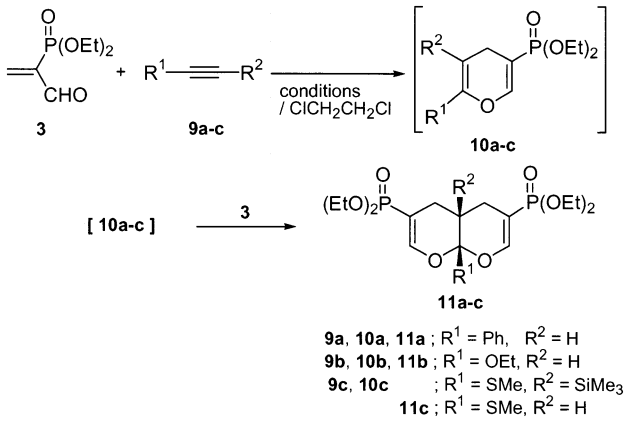


TABLE 4. Intermolecular Hetero Diels−Alder Reaction of 3 with Alkyne[a]

		reaction condition		product[b]
entry	Alkyne	temp.	time/h	(yield/%)
1	Ph−≡−H	reflux	5	**11a** (67)
2	EtO−≡−H	r.t.	5	**11b** (37)
3	MeS−≡−$SiMe_3$	reflux	5	**11c** (85)

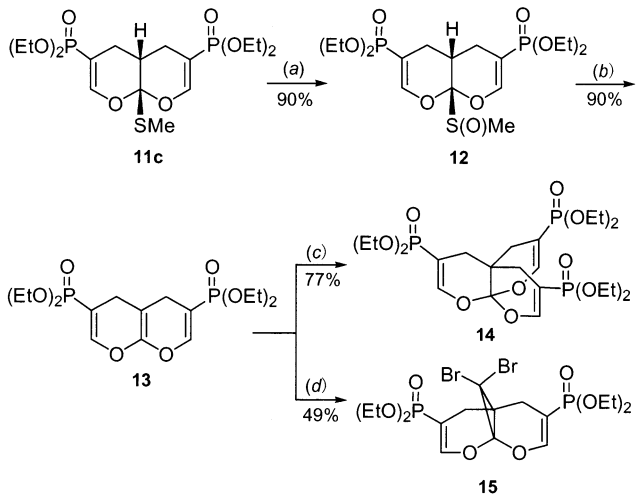
[a] All reactions were carried out in $ClCH_2CH_2Cl$ in the presence of 1.2 equiv of alkynes. [b] Isolated yield. Yield is based on **3**.

(13) For hetero-Cope rearrangement, see: Ismail, Z. M.; Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 859.

(14) Since the [4 + 2] adduct **7a** underwent hetero-Cope rearrangement to transform into the isomer **7b**, the compound **7a** was concluded to be the structure **7a** in which the aldehyde group situates in the endo position.

(15) Since the thermal elimination reaction of **12** produced **13** in good yield, R^1 and R^2 substituents of pyranopyran **11a**−**c** must be situated in the cis position (Scheme 4, path b).

SCHEME 4[a]



[a] Key: (a) *m*-CPBA (1.1 equiv), CH_2Cl_2, rt, 2 h; (b) toluene, reflux, 35 h; (c) **3** (3.0 equiv), toluene, reflux, 17 h; (d) K_2CO_3 and $CHBr_3$ (10.0 equiv each), 18-crown-6 (0.1 equiv), toluene, reflux, 8 h.

Alder adduct **14** was successfully produced in 77% yield (Scheme 4, path c). Furthermore, we investigated the possibility of [2 + 1] cyclization reaction by trapping carbene species[16] with **13**. The reaction of **13** with 10 equiv of bromoform was carried out at reflux for 8 h in toluene containing K_2CO_3 (10 equiv) and catalytic amounts of 18-crown-6 (0.1 equiv) to afford a hoped-for [2 + 1] cycloadduct **15** in 49% yield (Scheme 4, path d). Thus, we succeeded in the synthesis of a wide variety of phosphono-substituted pyrans using phosphonoacrolein **3**.

Conclusion. We note the following results from this investigation: (1) The first synthesis of phosphonoacrolein **3** was achieved by acidic decomposition of *β*-ethoxy-α-(methoxymethyl)vinylphosphonate. (2) The reaction of **3** with either alkenes or conjugated dienes gave [4 + 2] cycloadducts in which **3** acted to alkenes as a 4*π*-component and dienes as a 2*π*-component. (3) The reaction between **3** and alkynes afforded 2:1 [4 + 2] cycloadducts via the tandem hetero Diels−Alder reaction of 2 mol of **3** with alkynes.

Experimental Section

Materials. Dichloromethane was distilled from P_2O_5. THF was distilled from sodium benzophenone ketyl in a recycling still. Diisopropylamine (DIA), 1,2-dichloroethane, and toluene were refluxed with CaH_2 and then distilled. A commercial solution of ^{n}BuLi (1.50 M in hexane) was used. The starting material **1** was prepared according to the established procedures.[17]

General Methods. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ or C_6D_6, ^{1}H NMR at 400.13 and 500.00 MHz and ^{13}C NMR at 100.61 and 125.65 Hz, with Me_4Si as an internal standard unless otherwise noted. Infrared spectra were recorded of thin films on KBr plates. Mass spectra were recorded at 70 eV by GC inlet or by direct inlet for the thermally labile products. Melting points were measured in open capillary tubes and are uncorrected.

Preparation of Diethyl α-(Methoxymethyl)vinylphosphonate (2). To a solution of LDA, generated in situ from DIA (0.84 mL, 6.10 mmol) in THF (40.0 mL) and ^{n}BuLi (1.50 M in hexane, 4.60 mL, 7.30 mmol) at −78 °C for 1.0 h under nitrogen atmosphere, was added dropwise a solution of diethyl (*E*)-2-(ethoxy)vinylphosphonate (**1**) (1.28 g, 6.14 mmol) in THF (5.00 mL). After the mixture was stirred at this temperature for 1.0 h, methoxymethyl chloride (0.69 mL, 9.21 mmol) was added, and the reaction mixture was stirred for 1.0 h. The reaction was quenched by the addition of phosphate buffer (pH = 7), and the organic layer was extracted with AcOEt, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel (AcOEt/$CHCl_3$ = 1:2) to give **2** (1.11 g, 4.30 mmol, 70%) as a yellow oil: IR 2983, 1633, 1213, 1093, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (6H, t, J = 7.0 Hz), 1.32 (3H, t, J = 7.0 Hz), 3.32 (3H, s), 4.02−4.10 (8H, m), 7.19 (1H, d, $^3J_{P-H}$ = 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 15.2, 16.2 (d, $^3J_{P-C}$ = 7.1 Hz), 57.8, 61.4 (d, $^2J_{P-C}$ = 4.1 Hz), 64.1 (d, $^2J_{P-C}$ = 5.2 Hz), 100.6 (d, $^1J_{P-C}$ =193.2 Hz), 162.4 (d, $^2J_{P-C}$ = 27.9 Hz); HRMS calcd for $C_{10}H_{21}O_5P$ 252.1127 (M^+), found 252.1100.

Synthesis of Diethyl α-Formylvinylphosphonate (3). Procedure A. A solution of **2** (69.2 mg, 0.28 mmol) in CF_3CO_2H (1.00 mL) containing H_2O (10.1 mg, 0.56 mmol) was stirred at room temperature for 3 h. The organic layer was concentrated in vacuo to give **3** (53.8 mg, 0.28 mmol, >99%) as a yellow oil.

Procedure B. To a solution of **2** (130 mg, 0.52 mmol) in CH_2Cl_2 (3.00 mL) containing H_2O (18.6 mg, 1.03 mmol) was added excess Nafion NR-50 or AMBERLYST 15 (670 mg). The mixture was stirred at room temperature for 24 or 12 h. After removal of solid acids by filtration, the organic layer was concentrated in vacuo to give **3** (98.1 mg, 0.51 mmol, 99%) as a yellow oil: IR 2989, 1702, 1635, 1216 cm^{-1}; ^{1}H NMR ($CDCl_3$ + C_6D_6 + CCl_4) δ 1.37 (6H, t, J = 7.0 Hz), 4.18−4.23 (4H, m), 6.88 (1H, d, $^3J_{P-H}$ = 43.5 Hz), 7.24 (1H, d, $^3J_{P-H}$ = 20.1 Hz), 9.63 (1H, d, $^3J_{P-H}$ = 22.0 Hz); ^{13}C NMR ($CDCl_3$ + C_6D_6 + CCl_4) δ 16.0 (d, $^3J_{P-C}$ = 6.3 Hz), 63.2 (d, $^2J_{P-C}$ = 6.3 Hz), 139.9 (d, $^1J_{P-C}$ = 181.9 Hz), 147.6 (d, $^2J_{P-C}$ = 7.3 Hz), 187.7 (d, $^2J_{P-C}$ = 9.3 Hz); MS (FAB+) *m*/*z* 193 (M^+ + H); HRMS (FAB+) calcd for $C_7H_{14}O_4P$ 193.0629 (M^+ + H), found 193.0635.

[4 + 2] Cycloaddition Reaction of 3 with Alkenes 4a−f. General Procedure. A solution of **3** (49.2 mg, 0.237 mmol) and an alkene **4** (0.284 mmol) in $ClCH_2CH_2Cl$ (2.40 mL) or Et_2O was stirred at room temperature or at refluxing temperature for 3−10 h. After removal of solvent, the residue was chromatographed on silica gel (AcOEt/$CHCl_3$ = 1:4) to give **5a**−**d** or **6e**,**f**. The reaction conditions and yields of **5a**−**d** and **6e**,**f** were summarized in Table 2 and Scheme 1. The compounds **5a**−**d** and **6e**,**f** had the following properties.

[4 + 2] Cycloaddition Reaction of 3 with Alkenes 4a,d in the Presence of BF_3·OEt_2. General Procedure. A solution of **3** (60.0 mg, 0.289 mmol), an alkene **4** (0.347 mmol), and BF_3·Et_2O (0.048 mL, 0.376 mmol) in $ClCH_2CH_2Cl$ (2.40 mL) was stirred at refluxing temperature for 6−11 h. After removal of solvent, the residue was chromatographed on silica gel (AcOEt/$CHCl_3$ = 1:4) to give **5a**,**d**. The reaction conditions and yields of **5a**,**d** were summarized in Table 2 and Scheme 1. The compounds **5a**,**d** had the following properties.

5-(Diethylphosphono)-3,4-dihydro-2-phenyl-2*H*-pyran (5a): colorless oil; IR 3467, 2981, 2929, 1625, 1245 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (3H, t, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz), 1.83−1.91 (1H, m), 2.05−2.15 (2H, m), 2.21−2.26 (1H, m), 3.95−4.06 (4H, m), 4.87 (1H, dd, J = 2.5, 10.5 Hz), 7.25−7.32 (6H, m); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, $^3J_{P-C}$ = 6.3 Hz), 16.4 (d, $^3J_{P-C}$ = 6.2 Hz), 19.8 (d, $^2J_{P-C}$ = 6.3 Hz), 28.8 (d, $^2J_{P-C}$ = 10.3 Hz), 61.4 (d, $^2J_{P-C}$ = 6.3 Hz), 77.8, 98.8 (d, $^1J_{P-C}$ = 198.4 Hz), 125.7, 128.1, 128.5, 140.2, 155.4 (d, $^2J_{P-C}$ = 24.9

(16) For generation and synthetic applications of dibromocarbene, see, for example: Fedorynski, M.; Wojciechowski, K. et al. *J. Org. Chem*. **1978**, *43*, 4682.

(17) For a synthetic application of *β*-oxy or *β*-thio-substituted vinylphosphonates, see: Kouno, R.; Okauchi, T.; Nakamura, M.; Ichikawa, J.; Minami, T. *J. Org. Chem*. **1988**, *63*, 6239.

Hz). Anal. Calcd for $C_{15}H_{21}O_4P$: C, 60.80; H, 7.17. Found: C, 60.80; H, 7.14.

5-(Diethylphosphono)-3,4-dihydro-2-ethoxy-2*H*-pyran (5b): colorless oil; IR 3448, 2979, 2931, 1629, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (3H, t, J = 7.0 Hz), 1.32 (6H, t, J = 6.5 Hz), 1.77−1.84 (1H, m), 1.90−1.95 (1H, m), 2.05−2.12 (1H, m), 2.20−2.27 (1H, m), 3.59−3.64 (1H, m), 3.82−3.87 (1H, m), 4.03−4.08 (4H, m), 5.10 (1H, t, J = 2.4 Hz), 7.07 (1H, d, $^3J_{P-H}$ = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.5, 15.3 (d, $^3J_{P-C}$ = 6.3 Hz), 15.7 (d, $^3J_{P-C}$ = 8.3 Hz), 15.8 (d, $^3J_{P-C}$ = 8.3 Hz), 25.3 (d, $^2J_{P-C}$ = 10.3 Hz), 60.9 (d, $^2J_{P-C}$ = 4.2 Hz), 61.0 (d, $^2J_{P-C}$ = 4.2 Hz), 63.6, 96.7, 99.1 (d, $^1J_{P-C}$ = 198.4 Hz), 152.0 (d, $^2J_{P-C}$ = 24.8 Hz). Anal. Calcd for $C_{11}H_{21}O_5P$: C, 50.00; H, 8.01. Found: C, 49.99; H, 7.96.

3-(Diethylphosphono)-4,4a,5,6,7,8a-hexahydro-1,8-dioxanaphthalene (5c): colorless oil; IR 3450, 2933, 2868, 1631 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (6H, t, J = 6.7 Hz), 1.52−1.63 (4H, m), 1.92−1.94 (1H, m), 2.02−2.03 (1H, m), 2.28−2.32 (1H, m), 3.62−3.64 (1H, m), 3.78−3.80 (1H, m), 3.95−4.03 (4H, m), 5.15 (1H, d, J = 2.6 Hz), 7.04 (1H, dd, $^3J_{P-H}$ = 10.6 Hz, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, $^3J_{P-C}$ = 7.3 Hz), 23.3, 24.0, 24.9 (d, $^2J_{P-C}$ = 5.7 Hz), 30.9 (d, $^3J_{P-C}$ = 9.3 Hz), 61.5 (d, $^2J_{P-C}$ = 5.2 Hz), 61.8 (d, $^2J_{P-C}$ = 36.2 Hz), 97.3 (d, $^1J_{P-C}$ = 199.5 Hz), 98.1, 153.2 (d, $^2J_{P-C}$ = 22.7 Hz); MS m/z 276 (M^+). Anal. Calcd for $C_{12}H_{21}O_5P$: C, 52.17; H, 7.66. Found: C, 52.49; H, 7.72.

5-(Diethylphosphono)-3,4-dihydro-2-phenylthio-2*H*-pyran (5d): colorless oil; IR 3336, 2977, 2935, 1625, 1457 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (3H, t, J = 6.9 Hz), 1.35 (3H, t, J = 7.0 Hz), 2.14−2.30 (4H, m), 4.03−4.13 (4H, m), 5.57 (1H, t, J = 4.3 Hz), 7.12 (1H, d, $^3J_{P-H}$ = 10.8 Hz), 7.30−7.35 (3H, m), 7.50−7.52 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.7 (d, $^3J_{P-C}$ = 6.3 Hz), 17.3 (d, $^3J_{P-C}$ = 6.5 Hz), 26.4 (d, $^2J_{P-C}$ = 10.1 Hz), 62.5 (d, $^3J_{P-C}$ = 6.1 Hz), 62.6 (d, $^3J_{P-C}$ = 6.4 Hz), 99.0 (d, $^1J_{P-C}$ = 202.3 Hz), 127.9, 129.0, 132.2, 132.7, 153.8 (d, $^2J_{P-C}$ = 25.6 Hz); MS m/z 328 (M^+). Anal. Calcd for $C_{15}H_{21}O_4PS$: C, 55.17; H, 6.63. Found: C, 54.87; H, 6.45.

5-(Diethylphosphono)-3,4-dihydro-2,2-diethylthio-2*H*-pyran (6e): yellow oil.; IR 3453, 2977, 2929, 1629, 1444 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (6H, t, J = 7.5 Hz), 1.34 (6H, t, J = 7.0 Hz), 2.26−2.31 (4H, m), 2.74 (2H, q, J = 7.5 Hz), 2.75 (2H, q, J = 7.5 Hz), 4.04−4.19 (4H, m), 7.05 (1H, d, $^3J_{P-H}$ = 10.8 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.3 (d, $^3J_{P-C}$ = 6.5 Hz), 18.8 (d, $^3J_{P-C}$ = 6.1 Hz), 24.1, 32.8 (d, $^2J_{P-C}$ = 10.1 Hz), 61.6 (d, $^3J_{P-C}$ = 5.1 Hz), 94.3, 101.2 (d, $^1J_{P-C}$ = 196.1 Hz), 152.3 (d, $^2J_{P-C}$ = 25.8 Hz). Anal. Calcd for $C_{13}H_{25}O_4PS_2$: C, 45.86; H, 7.40. Found: C, 46.02; H, 7.36.

5-(Diethylphosphono)-3,4-dihydro-3,3-dimethyl-2-hydroxy-2*H*-pyran (6f): white solid; mp 74−75 °C; IR 3450, 2970, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3H, s), 1.01 (3H, s, J = 7.0 Hz), 1.32 (3H, t, J = 7.0 Hz), 1.32 (3H, t, J = 7.0 Hz) 1.72−1.77 (1H, m), 2.07−2.08 (1H, m), 3.99−4.08 (4H, m), 4.93 (1H, s), 5.55 (1H, d, J = 3.0 Hz) 7.02 (1H, d, $^3J_{P-H}$ = 10.8 Hz); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, $^3J_{P-C}$ = 4.8 Hz), 23.5, 23.9, 30.0 (d, $^3J_{P-C}$ = 4.7 Hz), 31.5 (d, $^2J_{P-C}$ = 9.3 Hz), 61.4 (d, $^2J_{P-C}$ = 5.0 Hz), 61.5 (d, $^2J_{P-C}$ = 7.7 Hz), 98.4 (d, $^1J_{P-C}$ = 196.9 Hz), 98.5, 152.4 (d, $^2J_{P-C}$ = 25.3 Hz). Anal. Calcd for $C_{11}H_{21}O_5P$: C, 50.00; H, 8.00. Found: C, 49.71; H, 8.01.

[4 + 2] Cycloaddition Reaction of 3 with Dienes. General Procedure. A solution of **3** (391.7 mg, 2.01 mmol) and cyclopentadiene or cyclohexadiene (10.1 mmol) in toluene (2.10 mL) was stirred at 0−110 °C for 10 h. After removal of solvent, the residue was chromatographed on silica gel (AcOEt/$CHCl_3$ = 1:2) to give **7a**,**b** or **8a**,**b**. The reaction conditions and yields of **7a**,**b** and **8a**,**b** were summarized in Scheme 2 and Table 3. The compounds **7a**,**b** and **8a**,**b** had the following properties.

5-(Diethylphosphono)-5-formylbicyclo[2.2.1]hept-2-ene (7a): colorless oil; IR 3482, 3409, 2975, 2931, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (3H, t, J = 6.9 Hz), 1.34 (1H, m), 1.37 (3H, t, J = 7.0 Hz), 1.98 (1H, m), 2.07−2.09 (1H, m), 2.12−2.25 (1H, m), 3.00 (1H, m), 3.54 (1H, m), 4.11−4.26 (4H, m), 6.06 (1H, dd, J = 2.7, 5.4 Hz), 6.20 (1H, dd, J = 3.2, 5.5 Hz), 9.47 (1H, s); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, $^3J_{P-C}$ = 5.6 Hz), 16.4 (d, $^3J_{P-C}$ = 5.7 Hz), 30.9, 43.2 (d, $^2J_{P-C}$ = 2.3 Hz), 46.8 (d, $^2J_{P-C}$ = 3.2 Hz), 47.4, 60.6 (d, $^1J_{P-C}$ = 130.4 Hz), 62.5 (d, $^2J_{P-C}$ = 7.4 Hz), 62.8 (d, $^2J_{P-C}$ = 7.0 Hz), 133.2 (d, $^3J_{P-C}$ = 13.7 Hz), 140.0, 197.3 (d, $^2J_{P-C}$ = 4.3 Hz); MS (FAB+) m/z 259 (M^+ + H); HRMS (FAB+) calcd for $C_{12}H_{20}O_4P$ 259.1087 (M^+ + H), found 259.1098. Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.81; H, 7.42. Found [for a mixture of **7a** and **7b**]: C, 55.65; H, 7.47.

4-(Diethylphosphono)-2-oxabicyclo[4.3.0]nona-3,8-diene (7b): colorless oil; IR 3471, 2981, 1631, 1241 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26−1.37 (6H, m), 1.95−2.07 (1H, m), 2.21−2.30 (1H, m), 2.32−2.43 (1H, m), 2.54−2.59 (2H, m), 4.01−4.11 (4H, m), 4.92 (1H, d, J = 5.6 Hz), 5.89−5.92 (1H, m), 6.04 (1H, dd, J = 2.8, 2.9 Hz), 7.27 (1H, d, ^3J = 10.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, $^3J_{P-C}$ = 6.5 Hz), 20.7 (d, $^3J_{P-C}$ = 5.7 Hz), 34.2 (d, $^2J_{P-C}$ = 8.7 Hz), 37.5, 61.2 (d, $^2J_{P-C}$ = 5.1 Hz), 81.0, 95.3 (d, $^1J_{P-C}$ = 201.0 Hz), 131.7, 135.8, 156.3 (d, $^2J_{P-C}$ = 25.0 Hz). Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.81; H, 7.42. Found [for a mixture of **7a** and **7b**]: C, 55.65; H, 7.47.

5-(Diethylphosphono)-5-formylbicyclo[2.2.2]oct-2-ene (8a): colorless oil; IR 3467, 2944, 1724, 1444, 1247 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21−1.25 (2H, m), 1.28 (3H, t, J = 7.1 Hz), 1.36 (3H, t, J = 7.1 Hz), 1.68−1.71 (1H, m), 1.89 (1H, ddd, J = 2.2, 2.2, 13.1 Hz), 2.17−2.20 (1H, m), 2.35−2.40 (1H, m), 2.70 (1H, s) 3.27 (1H, s), 4.07−4.24 (4H, m), 6.15 (1H, t, J = 7.6 Hz), 6.27 (1H, t, J = 7.4 Hz), 9.35 (1H, s); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, $^3J_{P-C}$ = 6.2 Hz), 16.4 (d, $^3J_{P-C}$ = 6.2 Hz), 21.5 (d, $^3J_{P-C}$ = 2.1 Hz), 24.5, 29.3, 30.0 (d, $^2J_{P-C}$ = 4.2 Hz), 32.5 (d, $^2J_{P-C}$ = 2.2 Hz), 57.6 (d, $^1J_{P-C}$ = 129.2 Hz), 62.5 (d, $^2J_{P-C}$ = 7.2 Hz), 62.6 (d, $^2J_{P-C}$ = 6.2 Hz), 132.0 (d, $^3J_{P-C}$ = 16.4 Hz), 136.5, 198.0; MS (FAB+) m/z 273 (M^+ + H).

4-(Diethylphosphono)-2-oxabicyclo[4.3.0]deca-3,9-diene (8b): colorless oil; IR 3424, 2981, 2925, 1627, 1234 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30−1.37 (6H, m), 1.56−1.59 (1H, m), 1.67−1.69 (1H, m), 1.95 (1H, ddd, J = 7.3, 7.6, 16.8 Hz), 2.04−2.25 (3H, m) 2.32−2.38 (1H, m), 4.04−4.08 (4H, m), 4.44 (1H, s), 5.83−5.85 (1H, m), 5.94−5.97 (1H, m), 7.12 (1H, d, ^3J = 10.6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, $^3J_{P-C}$ = 6.2 Hz), 16.3 (d, $^3J_{P-C}$ = 6.3 Hz), 23.0, 23.9 (d, $^3J_{P-C}$ = 5.2 Hz), 24.7, 29.4 (d, $^2J_{P-C}$ = 9.3 Hz), 61.3 (d, $^2J_{P-C}$ = 5.2 Hz), 70.7, 96.6 (d, $^1J_{P-C}$ = 198.4 Hz), 125.4, 132.8, 153.6 (d, $^2J_{P-C}$ = 23.7 Hz); MS (FAB+) m/z 273 (M^+ + H); HRMS (FAB+) calcd for $C_{13}H_{22}O_4P$ 273.1254 (M^+ + H), found 273.1263.

Thermal Transformation of 7a into 7b. A solution of **7a** (20.0 mg, 0.0770 mmol) in toluene (1.00 mL) was heated at refluxing temperature for 3 h. After removal of solvent, the residue was chromatographed on silica gel (AcOEt/$CHCl_3$ = 1:2) to give **7b** (18.0 mg, 0.070 mmol, 90%).

Thermal Transformation of 7a in the Presence of 4d. A mixture of **7a** (65.3 mg, 0.252 mmol) and **4d** (0.329 mL, 2.52 mmol) in $ClCH_2CH_2Cl$ (2.6 mL) was heated at refluxing temperature for 6.5 h. After similar workup, the residue was chromatographed on silica gel (AcOEt/$CHCl_3$ = 1:2) to give **7b** (60.0 mg, 0.232 mmol, 92%).

[4 + 2] Cycloaddition Reaction of 3 with Alkynes 9a−c. General Procedure. A solution of **3** (46.5 mg, 0.242 mmol) and an alkyne **9** (0.291 mmol) in $ClCH_2CH_2Cl$ (2.40 mL) was stirred at room temperature or refluxing temperature for 5 h. After conventional workup, the residue was chromatographed on silica gel (AcOEt/$CHCl_3$ = 1:2) to give **11a**−**c**. The reaction conditions and yields of **11a**−**c** were summarized in Table 4. The compound **11a**−**c** had the following properties.

3,6-Bis(diethylphosphono)-4,4a,5,8a-tetrahydro-4a-phenyl-1,8-dioxanaphthalene (11a): colorless solid; mp 65−66 °C; IR 3475, 2983, 2915, 1685, 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (6H, m), 1.32 (3H, t, J = 7.1 Hz), 1.32 (3H, t, J = 7.1 Hz), 2.12 (4H, s), 2.69 (1H, m), 4.03−4.09 (8H, m), 7.16 (2H, d, $^3J_{P-C}$ = 10.5 Hz), 7.39−7.44 (5H, m); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, $^3J_{P-C}$ = 11.3 Hz), 22.8 (m), 30.7 (dd, $^3J_{P-C}$ = 9.7, 9.8 Hz), 61.9 (d, $^2J_{P-C}$ = 11.3 Hz), 100.5 (d, $^1J_{P-C}$ = 203.1 Hz),

100.7, 125.2, 128.6, 129.5, 137.6, 151.2 (d, $^2J_{P-C}$ = 22.7 Hz); MS (FAB+) *m*/*z* 487 (M^+ + H). Anal. Calcd for $C_{22}H_{32}O_8P_2$: C, 54.32; H, 6.63. Found: C, 54.17; H, 6.56.

3,6-Bis(diethylphosphono)-4,4a,5,8a-tetrahydro-4a-ethoxy-1,8-dioxanaphthalene (11b): colorless oil; IR 3470, 2981, 2933, 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (3H, t, J = 7.3 Hz), 1.33 (12H, t, J = 7.0 Hz), 2.01−2.10 (2H, m), 2.28−2.35 (1H, m,) 2.36−2.44 (2H, m), 3.85 (2H, q, J = 7.0 Hz), 4.02−4.10 (8H, m), 6.93 (2H, d, $^3J_{P-H}$ = 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 15.1, 16.2 (d, $^3J_{P-C}$ = 6.2 Hz), 16.3 (d, $^3J_{P-C}$ = 6.2 Hz), 23.8, 30.4 (dd, $^3J_{P-C}$ = 9.3, 10.3 Hz), 58.1, 61.7 (d, $^2J_{P-C}$ = 5.1 Hz), 100.4 (d, $^1J_{P-C}$ = 197.4 Hz), 110.8, 150.1 (d, $^2J_{P-C}$ = 25.9 Hz); MS (FAB+) *m*/*z* 455 (M^+ + H); HRMS (FAB+) calcd for $C_{18}H_{33}O_9P_2$ 455.1598 (M^+ + H), found 455.1618.

3,6-Bis(diethylphosphono)-4,4a,5,8a-tetrahydro-4a-methylthio-1,8-dioxanaphthalene (11c): colorless oil; IR 3469, 2983, 2931, 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (6H, t, J = 7.0 Hz), 1.34 (6H, t, J = 7.0 Hz), 2.04−2.10 (2H, m), 2.28 (3H, s), 2.38−2.43 (3H, m), 4.02−4.13 (8H, m), 6.94 (2H, d, $^3J_{P-H}$ =10.6 Hz); ^{13}C NMR ($CDCl_3$) δ 9.91, 16.2 (d, $^3J_{P-C}$ = 6.2 Hz), 23.8, 31.2 (dd, $^2J_{P-C}$ = 9.9, 9.9 Hz), 61.78 (d, $^2J_{P-C}$ = 5.1 Hz), 61.63 (d, $^2J_{P-C}$ = 5.1 Hz), 99.9 (d, $^1J_{P-C}$ = 197.6 Hz), 107.6, 149.5 (d, $^2J_{P-C}$ = 24.8 Hz); MS *m*/*z* 456 (M^+). Anal. Calcd for $C_{17}H_{30}O_8P_2S$: C, 44.73; H, 6.62. Found: C, 44.87; H, 6.89.

Oxidation of 11c. To a solution of **11c** (380.0 mg, 0.832 mmol) in CH_2Cl_2 (8.00 mL) was added *m*-CPBA (172.2 mg, 0.998 mmol) at room temperature, and then the mixture was stirred for 2 h. The reaction was quenched by the addition of phosphate buffer (pH = 7), and the organic layer was extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel (AcOEt/MeOH=15:1) to give **3,6-bis(diethylphosphono)-4,4a,5,8a-tetrahydro-4a-methylsulfinyl-1,8-dioxanaphthalene (12)** (353.9 mg, 0.748 mmol, 90%) as a white solid: mp 90−91 °C; IR 3468, 2963, 2930, 1643 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25−1.37 (12H, m), 2.15−2.23 (2H, m), 2.39−2.43 (1H, m), 2.68 (3H, s), 2.75−2.80 (1H, m), 2.81−2.90 (1H, m), 4.02−4.17 (8H, m), 6.92 (1H, dd, J = 1.5, 10.4 Hz), 7.12 (1H, dd, $^3J_{P-H}$ = 1.3, 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, $^3J_{P-C}$ = 6.0 Hz), 16.3 (d, $^3J_{P-C}$ = 6.0 Hz), 21.5 (d, $^2J_{P-C}$ = 5.2 Hz), 25.4 (dd, $^3J_{P-C}$ = 9.3, 9.3 Hz), 31.0, 62.0 (m), 102.0 (d, $^1J_{P-C}$ = 197.3 Hz), 102.5 (d, $^1J_{P-C}$ = 197.3 Hz), 106.9, 148.5 (d, $^2J_{P-C}$ = 24.8 Hz), 150.2 (d, $^2J_{P-C}$ = 24.8 Hz). Anal. Calcd for $C_{17}H_{30}O_9P_2S$: C, 43.22; H, 6.40. Found: C, 43.22; H, 6.28.

Thermal Decomposition of 12. A solution of **12** (350.0 mg, 0.740 mmol) in toluene (10.0 mL) was stirred at refluxing temperature for 35 h. After removal of solvent, the residue was chromatographed on silica gel (AcOEt/MeOH = 15:1) to give **3,6-bis(diethylphosphono)-4,5-dihydro-1,8-dioxanaphthalene (13)** (274.8 mg, 0.673 mmol, 90%) as a yellow solid: IR 3470, 2900, 1666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (6H, t, J = 7.1 Hz), 1.35 (6H, t, J = 7.0 Hz), 2.67 (4H, d, J = 3.4 Hz), 4.05−4.17 (8H, m), 6.95 (2H, d, $^3J_{P-H}$ = 10.8 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, $^3J_{P-C}$ = 6.7 Hz), 24.0 (d, $^2J_{P-C}$ = 7.3 Hz), 61.9 (d, $^2J_{P-C}$ = 5.5 Hz), 79.2 (dd, $^3J_{P-C}$ = 12.1, 12.1 Hz), 101.42 (d, $^1J_{P-C}$ = 194.7 Hz), 146.6, 149.2 (d, $^2J_{P-C}$ = 26.3 Hz). Anal. Calcd for $C_{16}H_{26}O_8P_2$: C, 47.06; H, 6.42. Found: C, 47.06; H, 6.44.

[4 + 2] Cycloaddition Reaction of 3 with Pyranopyran 13. A solution of **13** (39.0 mg, 0.095 mmol) and phosphonoacrolein **3** (57.7 mg, 0.300 mmol) in toluene (1.00 mL) was stirred at refluxing temperature for 17 h. After removal of solvent, the residue was chromatographed on silica gel (AcOEt/MeOH = 15:1) to give **4,8,13-Tris(diethylphosphono)-2,10,11-trioxatricyclo[4.4.4.0^{1,6}]tetradeca-3,8,12-triene (14)** (43.9 mg, 0.073 mmol, 77%) as a yellow oil: IR 3467, 2983, 2913, 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (9H, t, J = 7.0 Hz), 1.36 (9H, t, J = 7.0 Hz), 2.02−2.09 (3H, m), 2.42 (3H, dd, J = 2.01, 17.4 Hz) 4.08−4.16 (12H, m), 6.89 (3H, dd, $^3J_{P-H}$ = 10.8, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, $^3J_{P-C}$ = 6.1 Hz), 16.3 (d, $^3J_{P-C}$ = 6.2 Hz), 28.7 (m), 28.9 (m), 62.1 (d, $^2J_{P-C}$ = 5.1 Hz), 62.2 (d, $^2J_{P-C}$ = 4.5 Hz), 100.5 (d, $^1J_{P-C}$ = 198.9 Hz), 110.6, 147.9 (d, $^2J_{P-C}$ = 24.8 Hz); MS (FAB+) *m*/*z* 601 (M^+ + H); HRMS (FAB+) calcd for $C_{23}H_{40}O_{12}P_3$ 601.1738 (M^+ + H), found 601.1730.

[2 + 1] Cycloaddition Reaction of Pyranopyran 13 with Dibromocarbene. To a solution of **13** (75.0 mg, 0.184 mmol), $CHBr_3$ (0.161 mL, 1.84 mmol), and 18-crown-6 (5.0 mg, 0.0184 mmol) in toluene (2.00 mL) was added K_2CO_3 (254.3 mg, 1.84 mmol) at room temperature. The mixture was stirred at refluxing temperature for 8 h. After removal of solvent, the residue was chromatographed on silica gel (AcOEt/MeOH = 15:1) to give **11,11-dibromo-4,8-bis(diethylphosphono)-2,-10-dioxatricyclo[4.4.1.0^{1,6}]undeca-3,8-diene (15)** (53.0 mg, 0.091 mmol, 49%) as a white solid: mp 96−97 °C; IR 3465, 2987, 2910, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30−1.36 (12H, m), 2.62−2.66 (4H, m), 4.00−4.12 (8H, m), 7.06 (2H, d, $^3J_{P-H}$ = 11.4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2, 24.8 (dd, $^3J_{P-C}$ = 11.7, 12.1 Hz), 27.7 (d, $^3J_{P-C}$ = 7.6 Hz), 41.3, 61.9 (d, $^2J_{P-C}$ = 5.7 Hz), 62.0 (d, $^2J_{P-C}$ = 5.2 Hz), 81.6, 100.0 (d, $^1J_{P-C}$ = 198.9 Hz), 149.3 (d, $^2J_{P-C}$ = 25.8 Hz); MS (FAB+) *m*/*z* 579, 581, 583 (M^+ + H); HRMS (FAB+) calcd for $C_{17}H_{27}Br_2O_8P_2$ 578.9545, 580.9525, 582.9505 (M^+ + H), found 578.9551, 580.9503, 582.9539.

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Supporting Information Available: Spectral and analytical data for compounds **2**, **3**, **5a**−**d**, **6e**,**f**, **7a**,**b**, **8a**,**b**, **11a**−**c**, and **12**−**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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