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Lewis acid promoted cyclocondensations of α-ketophosphonoenoates with dienes—from Diels–Alder to hetero Diels–Alder reactions

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Dedicated to Professor Yoshito Kishi, recipient of the 2001 Tetrahedron Prize, wishing him the best in life and in chemistry

Abstract—The cycloaddition reaction between α-keto-β,γ-unsaturated phosphonates with cyclopentadiene, cyclohexadiene, dihydrofuran and dihydropyran in the presence of $SnCl_4$, affords hetero Diels–Alder products. The influence of substituents and reaction parameters were studied.

The reaction of α-keto-β,γ-unsaturated esters (alkoxycarbonyl-oxa-butadienes) with vinyl ethers constitutes a de novo synthesis of alkyl hex-4,5-enopyranosid uronates.[1,2] These cycloadditions have been regarded as inverse electron demand hetero Diels–Alder reactions[3] controlled by the LUMO of the so-called heterodiene. Sluggish reactions can be accelerated by pressure,[4] heat, or in the presence of Lewis acids,[1–5] which will lower the LUMO of the heterodiene by complexation with the carbonyl group.[1,6]

Asymmetric versions of this general reaction based on chiral oxazolidinones and a chiral mandelate ester have been reported by Tietz,[7] Brown,[8] and their coworkers, respectively.[9] A catalytic version employing bis(oxazoline)copper II complexes was reported by Evans and co-workers.[10] Variations including unsaturated β-keto sulfones[11] and α-methylene-β-keto sulfones[12] also have precedence. Little was known regarding the reaction of α-keto-β,γ-unsaturated phosphonates with alkenes in general when our work was initiated.[13] S. A. Evans and co-workers[14] reported on the reaction of diethyl α-crotonylphosphonates with enol ethers catalyzed by stannic chloride to afford the corresponding dihydropyran phosphonates. These authors favored a stepwise Mukaiyama–Michael sequence, followed by cyclization, rather than a hetero Diels–Alder cycloaddition pathway, primarily based on the stereochemistry of the major product. D. A. Evans and co-workers[10] have shown that the reaction of dimethyl α-crotonylphosphonate with a variety of enol ethers including dihydrofuran and dihydropyran, catalyzed by bis(oxazoline)copper complexes affords monocyclic and bicyclic cycloadducts, respectively, with good to excellent *endo*/*exo* ratios and high enantioselectivities for each isomer. Their mechanistic interpretation is consistent with an inverse electron demand Diels–Alder reaction, following a 'concerted asynchronous reaction' pathway, although a two-step process was not discounted. Diels–Alder reactions between cyclopentadiene and furan with γ-keto-α,β-unsaturated phosphonates have been reported with and without Lewis acid assistance.[15]

We report herein on the cycloaddition reaction of substituted dialkyl α-keto-β,γ-unsaturated phosphonates[16] with cyclopentadiene, cyclohexadiene, dihydrofuran and dihydropyran.

1. Results

In preliminary experiments we were intrigued that the reaction of diethyl α-crotonylphosphonate **1** with cyclopentadiene in the absence of Lewis acid catalysts led to the formation of the hetero Diels–Alder product **2** in addition to the normally expected cycloadduct **3** (Table 1). The ratio of products was highly in favor of **3** except when the reaction was done in water as solvent (Table 1, entries 7–9).[12] A higher *endo*/*exo* ratio for **3** was observed in water compared to non-polar aprotic solvents. Additives such as LiCl[17] or β-cyclodextrin,[18] as well as conducting the reaction at lower temperature in $CDCl_3$ did not change the ratios appreciably (Table 1, entries 4, 5 and 8, 9). The adduct **3** was susceptible to partial dephosphonylation affording the corresponding

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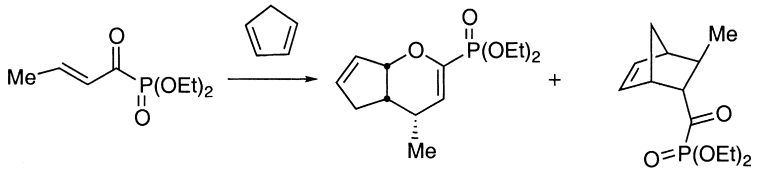
Table 1. Effect of the solvent in the reaction of α-keto phosphonoenoates **1** with cyclopentadiene



1 **2** **3**

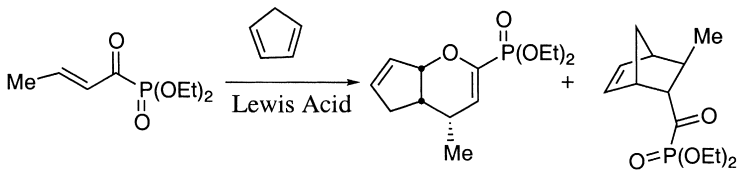
Entry	Solvent	Conditions[a], time (h)	3, *endo*/*exo*[b,c]	**2**/**3**[b]
1	Neat	RT, 8	6/1	1/6.6
2	Cyclohexane toluene	RT, 8	6.7/1	1/7.9
3	Toluene	RT, 20	7/1	1/10.3
4	$CDCl_3$	RT, 12	7/1	1/5.5
5	$CDCl_3$	−35°C, 72	10/1	1/5.5
6	CH_2Cl_2	RT, 17	1.4/1	1/8.8
7	H_2O	RT, 8	11/1	1/2
8	H_2O[d]	RT, 3.5	14.5/1	1/2.2
9	H_2O[e]	RT, 3	16/1	1/2.3

[a] All reactions were conducted with 2.8 equiv. of cyclopentadiene relative to **1**.
[b] Determined by ^{31}P NMR analysis directly on the crude reaction mixture.
[c] *endo*/*exo* ratio of **3**.
[d] 100 equiv. of LiCl relative to **1** were used.
[e] 1 equiv. of β-cyclodextrin relative to **1** was used.

carboxylic acid,[10,19] even under mild conditions of chromatographic purification.

We surveyed a series of Lewis acids[20] to assess their influence on the ratio of products and the overall rate of the reaction. The results for $Sc(OTf)_3$, $Yb(OTf)_3$, $BiCl_3$, $TiCl_4$, and $SnCl_4$ are summarized in Table 2. With $Sc(OTf)_3$ in acetonitrile, the time and temperature of the reaction were considerably reduced compared to non-catalyzed reactions. In general, a 2.8 mol/equiv. of cyclopentadiene and increasing equivalents of $Sc(OTf)_3$ were used. The α-keto-phosphonate **1** decomposed in aq. THF in the presence of the Lewis acid (Table 2, entry 1). In acetonitrile or methylene chloride increasing the equivalents of $Sc(OTf)_3$ resulted in a higher proportion of the hetero Diels–Alder product **2** (Table 2, entries 2–5). With $Yb(OTf)_3$, $BiCl_3$ and $TiCl_4$ in the same solvents, the ratios of **2** and **3** did not vary appreciably, even in the presence of 30 mol% of Lewis acid (Table 2, entries 6–8). A high ratio of 8:1 of **2** to **3** was also seen when 50–60 mol% of $SnCl_4$ was used in methylene chloride (Table 2, entry 12). Based on these results, we studied the reaction of various β,γ-substituted analogs of acryloyl dialkyl phosphonates with cyclopentadiene in the presence of 0.6 equiv. of $SnCl_4$ to evaluate the influence of

Table 2. Effect of various Lewis acids on the reaction of α-keto phosphonoenoates **1** with cyclopentadiene

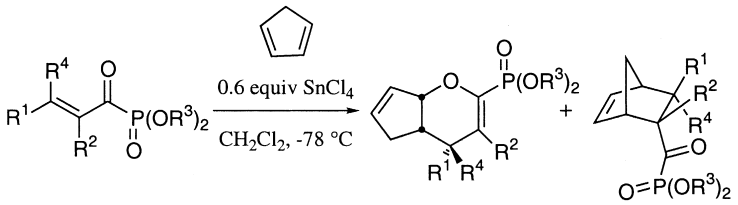


1 **2** **3**

Entry	Solvent	Conditions[a], time (h)	Lewis acid (mol%)	**2**/**3**[b]
1	THF/H_2O[c]	0°C, –[d]	$Sc(OTf)_3$ (10)	–[d]
2	CH_3CN	−40 to 0°C, 2.5	$Sc(OTf)_3$ (10)	1/1.4
3	CH_3CN	−40 to 0°C, 5	$Sc(OTf)_3$ (25)	3/1
4	CH_3CN	−40 to 0°C, 7	$Sc(OTf)_3$ (50)	9.3/1
5	CH_2Cl_2	−40 to 0°C, 3.5	$Sc(OTf)_3$ (50)	5/1
6	CH_3CN	−40 to 0°C, 5.5	$Yb(OTf)_3$ (25)	1/1.5
7	CH_3CN	−40 to 0°C, 6.5	$BiCl_3$ (25)	1/1.5
8	CH_2Cl_2	−78°C, 3	$TiCl_4$ (30)	2/1
9	CH_3CN	−50°C, 1.5	$SnCl_4$ (30)	2.5/1
10	CH_2Cl_2	−78°C, 3	$SnCl_4$ (30)	2.4/1
11	CH_2Cl_2	−78°C, 3	$SnCl_4$ (50)[e]	6/1
12	CH_2Cl_2	−78°C, 1.5	$SnCl_4$ (60)	8/1

[a] All reactions were conducted with with 2.8 equiv. of cyclopentadiene relative to **1**.
[b] Determined by ^{31}P NMR analysis directly on the crude reaction mixture.
[c] THF/H_2O: 9/1.
[d] **1** decomposed under these conditions.
[e] See Table 3 for *endo*/*exo* ratio.

Table 3. Reaction of α-keto phosphonoenoates **1** with cyclopentadiene in the presence of $SnCl_4$



1, 1a-e **2, 2a-e** **3, 3a-e**

Entry[a]	R^1	R^2	R^3	R^4	Product	Yield[b] (%) (*endo*/*exo*)[c] **2a–e**	**2/3**[c]
1	Me	H	Et	H	**2**	72 (20/1)	8/1
2	Me	H	Me	H	**2a**	74 (5.4/1)	>30/1
3	Me	H	*i*Pr	H	**2b**	52 (18/1)	3.6/1
4	Ph	H	Et	H	**2c**	77 (47/1)	7.5/1
5	Me	Me	Et	H	**2d**	59 (2.4/1)	2.4/1
6	Me	H	Et	Me	**2e**	61 (–)	15/1

[a] All reactions were conducted with 2.8 equiv. of diene relative to **1**.
[b] Isolated yield of **2**.
[c] Determined by ^{31}P NMR analysis directly on the crude reaction mixture.

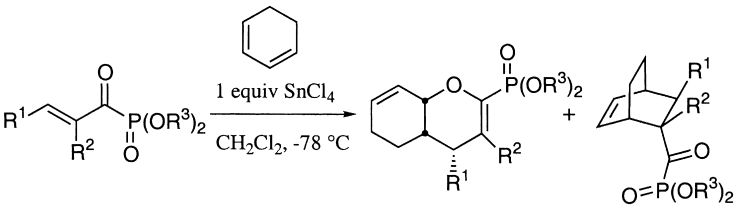
steric effects on the proportion of the hetero Diels–Alder and Diels–Alder products corresponding to **2** (Table 3).

With dimethyl α-crotonylphosphonate **1a**, the major product was **2a** based on nOe data (>30:1 compared to 8:1 for the diethyl ester, Table 3, entry 2). That the size of the ester group had an influence on the ratio of products **2** and **3** was evident in the case of the diisopropyl ester, where the proportion of Diels–Alder product **3b** was considerably higher compared to the dimethyl ester (Table 3, entries 2 and 3). In the case of diethyl α-cinnamoylphosphonate, the reaction appeared to still favor the hetero Diels–Alder product (Table 3, entry 4), while with the α-3,4-dimethyl-crotonyl analog, the ratio of products was only 2.4:1 in favor of **2** (Table 3, entries 4 and 5). Finally gem-dimethyl substitution at the terminal position of the olefin resulted in a substantial increase of the hetero Diels–Alder product (Table 3, entry 6). It is of interest that under these conditions the cycloadditions were consistently in favor of hetero Diels–Alder products with the *endo* product being the major isomer (Table 3, **2a–d**).

The reaction of dialkyl α-keto-β,γ-unsaturated phosphonates with cyclohexadiene was studied next. In the presence of 1 equiv. of $SnCl_4$, with the α-crotonyl and α-cinnamoyl esters, an almost equimolar amount of hetero Diels–Alder products **4** and **5** was observed with high *endo* selectivity for **4** based on nOe studies (Table 4, entries 1–3). The 3-substituted crotonylphosphonate however, strongly favored the hetero Diels–Alder product **4c** (Table 4, entry 4).

Finally, we studied the cyclocondensation of dialkyl α-crotonylphosphonates **1** and **1a–c** with dihydrofuran and dihydropyran. In both cases, the only isolable products were those arising from a hetero Diels–Alder condensation with high *endo*/*exo* ratios and good yields (Table 5, entries 1–4). Variations in the ester moiety or geminal substitution

Table 4. Reaction of α-keto phosphonoenoates **1** with cyclohexadiene in the presence of $SnCl_4$

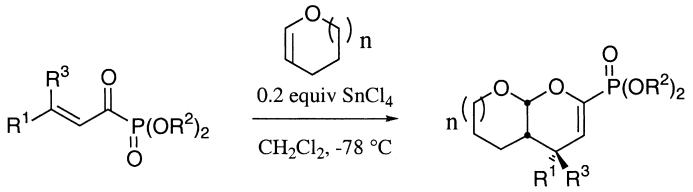


1, 1a-c **4, 4a-c** **5, 5a-c**

Entry	R^1	R^2	R^3	Product[a]	Yield[b] (%) (*endo*/*exo*)[c]	4/5[c]
1	Me	H	Et	**4**	43 (>50/1)[d]	1.1
2	Me	H	Me	**4a**	47 (>50/1)	1.2/1[d]
3	Ph	H	Et	**4b**	60 (32/1)	1.9/1
4	Me	Me	Et	**4c**	71 (17/1)	14/1

[a] All reactions were conducted with 5 equiv. of diene relative to **1**.
[b] Isolated yield of **4**.
[c] Determined by ^{31}P NMR analysis directly on the crude reaction mixture.
[d] 0.6 equiv. of $SnCl_4$ were used.

Table 5. Reaction of α-keto phosphonoenoates **1** with cyclic enol ethers in the presence of $SnCl_4$



1, 1a-c **6, 6a-c**

Entry	R^1	R^2	R^3	*n*	Product[a]	Yield[b] (%) (*endo*/*exo*)[c]
1	Me	Et	H	0	**6**	76 (25/1)
2	Me	Me	H	0	**6a**	78 (30/1)
3	Me	Et	Me	0	**6b**[d]	68 (–)[d,e]
4	Me	Me	H	1	**6c**[f]	77 (36/1)[f]

[a] All reactions were conducted with 5 equiv. of diene relative to **1**.
[b] Isolated yield of **6** and **6a–c**.
[c] Determined by ^{31}P NMR analysis directly on the crude reaction mixture.
[d] 0.5 equiv. of $SnCl_4$ were used.
[e] Two isomers (ratio 6.2/1).
[f] The reaction mixture was allowed to warm to −40°C.

did not adversely affect the stereochemical outcome of the reaction.

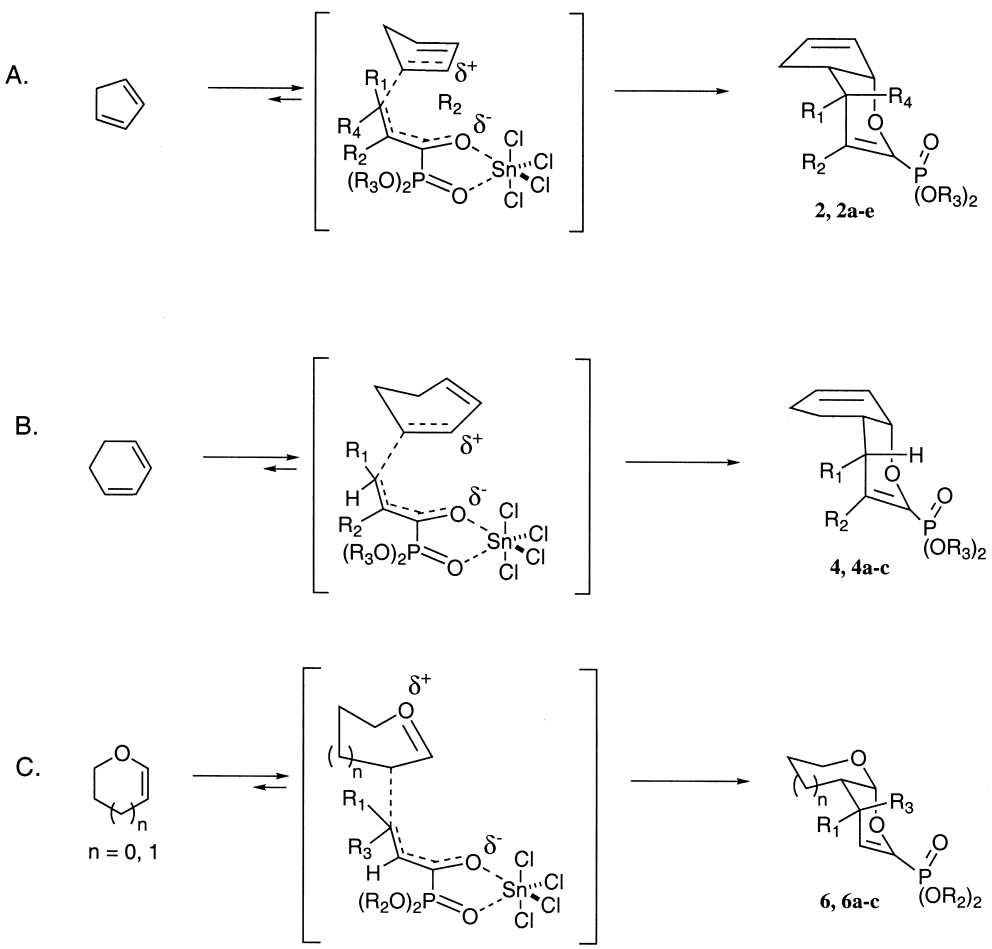
2. Discussion

The annals of the venerable Diels–Alder reaction contain a plethora of examples in which cyclopentadiene acts as the dienic partner in cycloaddition reactions with electron-deficient alkenes.[21] It was therefore surprising to find that the uncatalyzed reactions of cyclopentadiene with diethyl α-crotonylphosphonate **1** led to minor amounts of the hetero Diels–Alder product **2** (Table 1). Conducting the reaction in water with or without additives diminished the proportion of the Diels–Alder product **3**. The preponderance of *endo* adducts in the Diels–Alder reaction under aprotic conditions suggests that steric effects may predominate in the transition state. On the other hand hydration and miscellar effects may play a role in aqueous medium to increase the amount of hetero Diels–Alder product compared to non-aqueous solvents (Table 1, entries 7–9). The accelerating effect of Lewis acids in inverse electron demand cycloadditons is well known.[1–5] This is also manifested in the case in hand where increasing the amount of Lewis acid strongly favors the hetero Diels–Alder product (Table 2). Scheme 1 illustrates a probable pathway where the acyl phosphonate and the carbonyl group are coordinated with the Lewis acid.[14] The effect of *s-cis* and *s-trans* orientations of the phosphoryl acid mediated and carbonyl groups on the stereochemical outcome in related Lewis acid mediated reactions has been discussed by Evans and co-workers.[14] The effect of substituents can be rationalized by considering steric interactions in the transition-state and $A^{1,3}$-strain[22] (Scheme 1). In general, *endo*-substitution was prevalent (Table 3, entries 1–5). Vicinal substitution (as in **2d**) was detrimental to *endo*-selectivity as well as to the hetero Diels–Alder pathway (Table 3, entry 4). Increasing the bulk of the ester moiety also lowered the ratio of hetero to normal Diels–Alder products **2b** and **3b** (Table 3, entry 3) while geminal substitution as in **2e** favored the hetero Diels–Alder product (Table 3, entries 3 and 6). As reported by Boger[1] and Hoffmann[6] initially, complexation of the heterodiene with a Lewis acid lowers the LUMO energy and reverses the normal electron demand where cyclopentadiene acts as the dienophile.

The cycloaddition reaction with cyclohexadiene also follows a predictable course with regard to the high *endo*/*exo* selectivity for the hetero Diels–Alder product **4**, and **4a–c** (Table 4). The quasi equal ratio of normal [4+2] vs hetero variant Diels–Alder reaction is in strong contrast to the reaction with cyclopentadiene (Table 3). Here the vicinally dimethylated α-crotonylphosphonate **1c** led to the higher ratio of hetero Diels–Alder product **4c**, possibly because of the less favorable interactions in [2:2:2] substituted Diels–Alder product (Table 4, entry 4). Evidently, the crotonyl and cinnamoyl analogs are more subject to unfavorable non-bonded interaction in the tetrahydro-4*H*-chromene series compared to the tetrahydro oxaindene analogs (Scheme 1(B)).

The reaction of dialkyl α-crotonylphosphonates with electron rich olefins such as dihydrofuran and dihyropyran under $SnCl_4$ catalysis gave the hetero Diels–Alder products only, with a strong *endo*/*exo* preference (Table 5, entries 1–4). The possibility of zwitterionic intermediates arising from initial Michael attack of the dihydrofuran or pyran moiety is illustrated in Scheme 1(C), although a concerted mechanism cannot be excluded.

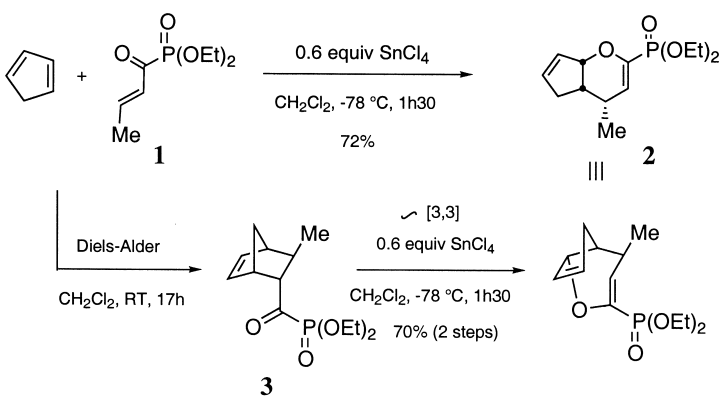
The reaction of electron rich vinyl ethers with α-keto-β,γ-unsaturated esters was shown to proceed by an inverse electron demand Diels–Alder reaction. Hoffmann[12] has alluded to the fact that the hetero Diels–Alder products arising from the uncatalyzed reaction of α-methylene-β-keto-sulfones with cyclopentadiene or cyclohexadiene can originate from a direct hetero [4+2] cycloaddition or by a retro-Claisen rearrangement of the 'normal' Diels–Alder adduct. As previously mentioned, treatment of **1** with cyclopentadiene afforded the expected Diels–Alder adduct **3** as a major product (Table 1, entry 6). When this product was treated with 0.6 equiv. of $SnCl_4$ at −78°C, we observed



Scheme 1.

a conversion to the hetero Diels–Alder product **2** in high yield (Scheme 2). Thus, the Hoffmann proposal[6,12] for a retro-Claisen [3+3] rearrangement[23] was experimentally verified in the reaction with cyclopentadiene and an α-crotonylphosphonate. The results obtained so far qualitatively argue in favor of a rearrangement pathway resulting from an initial [4+2] adduct, particularly when the amount of $SnCl_4$ is increased. When the size of the ester unit increases (Table 3, entries 1–3), the amount of hetero Diels–Alder products was significantly less. The trajectory of approach of the carbonyl group in a [3+3] Claisen rearrangement would be more susceptible to the size of the phosphonate ester group, compared to a normal [4+2] Diels–Alder reaction (Scheme 2). It is of interest that the product **3** was not converted to **2** in the presence of a copper bis-oxazoline catalyst.[10a]

In conclusion, we have shown that the reaction of α-keto-β,γ-unsaturated phosphonates undergo Lewis acid catalyzed cyclocondensation reactions to give hetero Diels–Alder products with cyclopentadiene, cyclohexadiene, dihydrofuran and dihydropyran with high *endo* selectivities. Diels–Alder cycloadducts appear to be initially formed with cyclopentadiene, which undergo



Scheme 2.

[3+3] Claisen rearrangement in the presence of a Lewis acid. These cyclocondensations are further examples of inverse electron demand hetero Diels–Alder reactions where the diene acts as a 2π component.

3. Experimental

3.1. General

^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ with $CHCl_3$ as reference. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ with $CHCl_3$ as reference and ^{31}P NMR at 121.4 MHz using 85% H_3PO_4 in D_2O as an external reference. Wherever necessary, ^{1}H NMR assignments were supported by appropriate homonuclear assignments (COSY). IR spectra were recorded neat. Mass spectra were recorded using electron ionization (EI) at 70 eV or by fast atom bombardment (FAB) techniques. Organic solvents were dried by standard methods. All reactions were performed under an inert atmosphere (dry N_2) and monitored by TLC with Merck 60 F_{254} silica gel coated plates. Flash chromatography was carried out using 230–400 mesh silica gel at increased pressure.

3.2. General procedure for the synthesis of oxabicyclic phosphonates (2, 2a–e, 4, 4a–c, 6, 6a–c)

To a 0.15 M solution of 1 equiv. of acyl phosphonates **1**, **1a–e** in CH_2Cl_2 at −78°C was added sequentially a 1 M solution of $SnCl_4$ (0.5–0.6 equiv. in CH_2Cl_2) and freshly distilled diene or enol ether (2.8 equiv. for cyclopentadiene, and 5 equiv. for cyclohexadiene, or dihydrofuran or dihydropyran). After the reaction was complete (1.5–8 h), the reaction mixture was quenched with a saturated solution of $NaHCO_3$ at −78°C. After extraction with CH_2Cl_2, the combined extracts were washed with a saturated solution of NaCl, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude oil was purified by flash chromatography on silica gel eluting with a mixture of hexanes and ethyl acetate.

3.2.1. (±)-(4*R-Methyl-4*R**,4a*S**,5,7a*R**-tetrahydro-cyclopenta[*b*]pyran-2-yl)-phosphonic acid diethyl ester (2).** From 0.08 g (0.38 mmol) of **1**[16b] and 89 μL (1.08 mmol) of cyclopentadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 1:1) **2** (76 mg, 0.28 mmol, 72%) as an oil. IR (neat) 1636, 1256, 1026 cm^{-1}; ^{1}H NMR δ 6.04 (m, 1H), 5.92 (m, 1H), 5.71 (m, 1H), 4.97 (m, 1H, *J*=6.6, 2.4, 1.3 Hz), 4.08 (m, 4H), 2.78 (m, 1H), 2.69 (m, 1H), 2.20 (m, 2H), 1.31 (m, 6H), 1.11 (d, 3H, *J*=7.1 Hz); ^{13}C NMR δ 146.2 (d, *J*=22.5 Hz), 137.2, 131.2, 121.7 (d, *J*=23.6 Hz), 83.2 (d, *J*=6.8 Hz),62.3 (d, *J*=4.7 Hz), 43.1 (d, *J*=2.4 Hz), 33.0, 26.5 (d, *J*=12.0 Hz), 17.9, 16.1; ^{31}P NMR δ +9.98; HRMS calcd for $C_{13}H_{22}O_4P$ 273.1262; found 273.1255.

3.2.2. (±)-(4*R-Methyl-4*R**,4a*S**,5,7a*R**-tetrahydro-cyclopenta[*b*]pyran-2-yl)-phosphonic acid dimethyl ester (2a).** From 0.24 g (1.35 mmol) of **1a** and 308 μL (3.74 mmol) of cyclopentadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2:1) **2a** (217 mg, 0.89 mmol, 66%) as an oil. IR (neat) 1635, 1259, 1028 cm^{-1}; ^{1}H NMR δ 6.08 (m, 1H), 5.92 (m, 1H), 5.75 (ddd, 1H, *J*=10.5, 2.5, 1.3 Hz), 5.00 (m, 1H), 3.70 (m, 6H), 2.82 (m, 1H), 2.76 (m, 1H), 2.26 (m, 2H), 1.10 (d, 3H, *J*=7.2 Hz); ^{13}C NMR δ 145.1 (d, *J*=226.2 Hz), 137.3, 131.1, 122.6 (d, *J*=23.7 Hz), 83.4 (d, *J*=6.7 Hz), 52.8, 43.7 (d, *J*=2.3 Hz), 32.9, 26.6 (d, *J*=12.0 Hz), 17.9; ^{31}P NMR δ +12.73; HRMS calcd for $C_{11}H_{18}O_4P$ 245.0942; found 245.0936.

3.2.3. (±)-(4*R-Methyl-4*R**,4a*S**,5,7a*R**-tetrahydro-cyclopenta[*b*]pyran-2-yl)-phosphonic acid diisopropyl ester (2b).** From 0.045 g (0.192 mmol) of **1b**[16b] and 44 μL (0.53 mmol) of cyclopentadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 1:1) **2b** (31 mg, 0.10 mmol, 52%) as an oil. ^{1}H NMR δ 6.03 (m, 1H), 5.98 (m, 1H), 5.68 (m, 1H), 4.96 (m, 1H), 4.62 (m, 2H), 2.78 (m, 1H), 2.62 (m, 1H), 2.23 (m, 2H), 1.32 (m, 12H), 1.10 (d, 3H, *J*=7.2 Hz); ^{13}C NMR δ 147.2 (d, *J*=22.5 Hz), 137.1, 131.3, 119.4 (d, *J*=23.8 Hz), 82.4 (d, *J*=6.8 Hz), 70.9, 43.0, 32.8, 26.3 (d, *J*=10.7 Hz), 23.9, 23.6, 19.7, 18.1; ^{31}P NMR δ+7.84; HRMS calcd for $C_{15}H_{26}O_4P$ 301.1568; found 301.576.

3.2.4. (±)-(4*R-Phenyl-4*R**,4a*S**,5,7a*R**-tetrahydro-cyclopenta[*b*]pyran-2-yl)-phosphonic acid diethyl ester (2c).** From 0.025 g (0.093 mmol) of **1c**[16c] and 21 μL (0.29 mmol) of cyclopentadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2:1) **2c** (24 mg, 0.07 mmol, 77%) as an oil. IR (neat) 1633, 1446, 1249, 1025, 763, 706 cm^{-1}; ^{1}H NMR δ 7.35–7.23 (m, 5H), 6.14 (m, 1H), 6.02 (m, 1H), 5.97 (m, 1H), 5.12 (m, 1H), 4.18 (m, 4H), 4.04 (m, 1H), 2.96 (m, 1H), 2.12 (m, 1H), 1.77 (m, 1H), 1.35 (m, 6H); ^{13}C NMR δ 147.9 (d, *J*=225.5 Hz), 141.6, 137.6, 130.8, 128.4, 127.5, 116.8 (d, *J*=24.5 Hz), 82.4 (d, *J*=7.2 Hz), 62.4 (d, *J*=5.3 Hz), 43.9 (d, *J*=2.3 Hz), 37.6, 37.5, 33.8, 16.2; ^{31}P NMR δ +9.50; HRMS calcd for $C_{18}H_{24}O_4P$ 335.1412; found 335.1421.

3.2.5. (3,4-Dimethyl-4,4a,5,7a-tetrahydro-cyclopenta[*b*]-pyran-2-yl)-phosphonic acid diethyl ester (2d). From 0.06 g (0.27 mmol) of **1d**[16d] and 62 μL (0.76 mmol) of cyclopentadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2:1) **2d** (46 mg, 0.161 mmol, 59%) as an oil obtained as a mixture of isomers (*endo*/*exo*=2.4/1). ^{1}H NMR δ 5.94 (m, 1H), 5.78 (m, 1H), 5.11 (m, 0.71H), 5.04 (m, 0.29H), 4.08 (m, 2.84H), 4.00 (m, 1.16H), 3.84 (m, 1H), 2.62 (m, 1.42H), 2.48 (m, 0.58H), 2.12 (m, 1H), 2.05 (m, 3H), 1.30 (m, 6H), 1.20 (d, 0.87H, *J*=7.1 Hz), 1.11 (d, 2.13H, *J*=7.2 Hz); ^{31}P NMR δ +10.55 (0.29); 10.45 (0.71); HRMS calcd for $C_{14}H_{24}O_4P$ 287.1412; found 287.1401.

3.2.6. (±)-(4,4-Dimethyl-4,4a*S,5,7a*R**-tetrahydro-cyclopenta[*b*]pyran-2-yl)-phosphonic acid diethyl ester (2e).** From 0.1 g (0.45 mmol) of **1e**[16c,e] and 103 μL (1.25 mmol) of cyclopentadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2/1) **2e** (79 mg, 0.28 mmol, 61%) as an oil. IR (neat) 1633, 1444, 1391, 1247, 1025 cm^{-1}; ^{1}H NMR δ 6.03 (m, 1H), 5.92 (m, 1H), 5.64 (dd, 1H, *J*=11.0, 1.5 Hz), 4.92 (m, 1H), 4.05 (m, 4H), 2.31–2.08 (m, 3H), 2.12 (m, 1H), 1.28 (m, 6H), 1.18 (s, 3H), 1.04 (s, 3H); ^{13}C NMR δ 145.7 (d, *J*=224.2 Hz), 137.3, 131.1, 123.5 (d, *J*=22.2 Hz), 80.5 (d, *J*=7.7 Hz),

62.2 (d, J=5.1 Hz), 49.0, 34.3, 30.4 (d, J=2.5 Hz), 30.3, 26.6, 16.1; ^{31}P NMR δ +10.47; HRMS calcd for $C_{14}H_{23}O_4P$ 287.1412; found 287.1411.

3.2.7. (±)-(4*R* *-Methyl-4a*S* *,5,6,8a*R* *-tetrahydro-4*H*-chromen-2-yl)-phosphonic acid diethyl ester (4). From 0.1 g (0.51 mmol) of **1** and 242 μL (2.54 mmol) of cyclohexadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2/1) **4** (63 mg, 0.22 mmol, 43%) as an oil. ^{1}H NMR δ 5.96 (m, 1H), 5.88 (m, 1H), 5.55 (m, 1H), 4.27 (m, 1H), 4.08 (m, 4H), 2.72 (m, 1H), 2.21 (m, 1H), 2.05 (m, 2H), 1.79 (m, 1H), 1.58 (m, 1H), 1.32 (m, 6H), 1.01 (d, 3H, J=7.4 Hz); ^{13}C NMR δ 142.5 (d, J=225.5 Hz), 133.5, 125.1, 118.9 (d, J=21.9 Hz), 71.8 (d, J=8.4 Hz), 62.3 (d, J=5.3 Hz), 35.6 (d, J=1.6 Hz), 29.6 (d, J=12.5 Hz), 26.1, 16.4, 16.2, 16.1; ^{31}P NMR δ +10.31; HRMS calcd for $C_{14}H_{24}O_4P$ 285.1255; found 285.1248.

3.2.8. (±)-(4*R* *-Methyl-4a*S* *,5,6,8a*R* *-tetrahydro-4*H*-chromen-2-yl)-phosphonic acid dimethyl ester (4a). From 0.1 g (0.56 mmol) of **1a** and 267 μL (2.81 mmol) of cyclohexadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2/1) **4a** (69 mg, 0.27 mmol, 47%) as an oil. ^{1}H NMR δ 6.01 (m, 1H), 5.91 (m, 1H), 5.62 (m, 1H), 4.29 (m, 1H), 3.76 (apparent t, 6H, J=10 Hz), 2.75 (m, 1H), 2.24 (m, 1H), 2.06 (m, 2H), 1.80 (m, 1H), 1.60 (m, 1H), 1.41 (m, 1H), 1.06 (d, 3H, J=7.1 Hz); ^{13}C NMR δ 141.5 (d, J=226.9 Hz), 133.8, 125.1, 119.8 (d, J=22.1 Hz), 72.0 (d, J=8.4 Hz), 52.9 (d, J=3.3 Hz), 35.7, 29.7 (d, J=12.7 Hz), 26.1, 16.5, 16.4; ^{31}P NMR δ +13.08; HRMS calcd for $C_{12}H_{20}O_4P$ 259.1099; found 259.1107.

3.2.9. (±)-(4*R* *-Phenyl-4a*S* *,5,6,8a*R* *-tetrahydro-4*H*-chromen-2-yl)-phosphonic acid diethyl ester (4b). From 0.055 g (0.20 mmol) of **1c** and 97 μL (1.02 mmol) of cyclohexadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2/1) **4b** (43 mg, 0.12 mmol, 60%) as an oil. IR (neat) 1634, 1603, 1494, 1452, 1252, 1025, 772, 704 cm^{-1}; ^{1}H NMR δ 7.34–7.14 (m, 5H), 5.96–5.91 (m, 3H), 4.52 (m, 1H), 4.18 (m, 4H), 4.05 (m, 1H), 2.18–2.01 (m, 3H), 1.88 (m, 1H), 1.38 (m, 6H), 0.98 (m, 1H); ^{13}C NMR δ 145.1 (d, J=225.5 Hz), 140.7, 133.8, 128.2, 128.0, 126.5, 124.8, 115.2 (d, J=23.1 Hz), 71.9 (d, J=8.3 Hz), 62.5 (d, J=5.4 Hz), 41.4 (d, J=12.7 Hz), 36.8, 26.1, 17.5, 16.2 (d, J=5.6 Hz); ^{31}P NMR δ +9.59; HRMS calcd for $C_{19}H_{26}O_4P$ 349.1568; found 349.1578.

3.2.10. (±)-(3,4*R* *-Dimethyl-4a*S* *,5,6,8a*R* *-tetrahydro-4*H*-chromen-2-yl)-phosphonic acid diethyl ester (4c). From 0.03 g (0.13 mmol) of **1d** and 64.9 μL (0.68 mmol) of cyclohexadiene was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 2/1) **4c** (30 mg, 0.10 mmol, 72%) as an oil. IR (neat) 1631, 1445, 1226, 1027 cm^{-1}; ^{1}H NMR δ 5.98 (m, 1H), 5.87 (m, 1H), 4.15 (m, 1H), 4.10 (m, 4H), 2.64 (m, 1H), 2.22 (m, 1H), 2.08 (m, 1H), 1.96 (apparent s, 3H), 1.82 (m, 1H), 1.63 (m, 1H), 1.34 (m, 6H), 1.32 (d, 3H, J=7.1 Hz); ^{13}C NMR δ 137.7 (d, J=225.6 Hz), 133.4, 126.2 (d, J=23.8 Hz), 125.3, 70.9 (d, J=7.8 Hz), 62.2, 37.3 (d, J=1.7 Hz), 34.8 (d, J=13.0 Hz), 26.2, 16.9, 16.2, 16.1, 14.9 (d, J=3.3 Hz), 14.5; ^{31}P NMR δ +11.54; HRMS calcd for $C_{15}H_{25}O_4P$ 300.1490; found 300.1482.

3.2.11. (±)-(4*R* *-Methyl-2,3,3a*S* *,7a*R* *-tetrahydro-4*H*-furo[2,3-*b*]pyran-6-yl)-phosphonic acid diethyl ester (6). From 0.055 g (0.26 mmol) of **1** and 101 μL (1.33 mmol) of 2,3-dihydro furan was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 1/2) **6** (56 mg, 0.20 mmol, 76%) as an oil. IR (neat) 1634, 1454, 1253, 1022 cm^{-1}; ^{1}H NMR δ 5.60 (m, 1H), 5.46 (d, 1H, J=3.9 Hz), 4.12 (m, 4H), 4.08 (m, 1H), 3.95 (m, 1H), 2.82 (m, 1H), 2.40 (m, 1H), 1.91 (m, 1H), 1.68 (m, 1H), 1.32 (m, 6H), 1.08 (d, 3H, J=7.3 Hz); ^{13}C NMR δ 142.1 (d, J=226.8 Hz), 117.4 (d, J=21.8 Hz), 101.2 (d, J=8.5 Hz), 68.1, 62.5, 62.4, 43.1, 26.6 (d, J=13.3 Hz), 23.3, 17.8, 16.2, 16.1; ^{31}P NMR δ +9.04; HRMS calcd for $C_{12}H_{21}O_5P$ 275.1048; found 275.1062.

3.2.12. (±)-(4*R* *-Methyl-2,3,3a*S* *,7a*R* *-tetrahydro-4*H*-furo[2,3-*b*]pyran-6-yl)-phosphonic acid dimethyl ester (6a). From 0.1 g (0.56 mmol) of **1a** and 212 μL (2.8 mmol) of 2,3-dihydrofuran was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 1/3) **6a** (110 mg, 0.44 mmol, 78%) as an oil. IR (neat) 1635, 1454, 1258, 1068, 1036 cm^{-1}; ^{1}H NMR δ 5.65 (ddd, 1H, J=11.3, 2.2, 1.4 Hz), 5.49 (d, 1H, J=3.9 Hz), 4.18 (m, 1H), 3.98 (m, 1H), 3.74 (apparent s, 3H), 3.72 (apparent s, 3H), 2.82 (m, 1H), 2.38 (m, 1H), 1.89 (m, 1H), 1.68 (m, 1H), 1.07 (d, 3H, J=7.3 Hz); ^{13}C NMR δ 141.1 (d, J=228.6 Hz), 118.3 (d, J=21.2 Hz), 101.2 (d, J=8.5 Hz), 68.2, 52.9, 43.1, 26.6 (d, J=13.5 Hz), 23.2, 17.7; ^{31}P NMR δ +11.81; LRMS calcd for $C_{10}H_{17}O_5P$ 249.2 (M+H); found 249.1.

3.2.13. (±)-(4,4-Dimethyl-2,3,3a*S* *,7a*R* *-tetrahydro-4*H*-furo[2,3-*b*]pyran-6-yl)-phosphonic acid diethyl ester (6b). From 0.13 g (0.59 mmol) of **1e** and 224 μL (2.95 mmol) of 2,3-dihydrofuran was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 1/1) **6b** (117 mg, 0.40 mmol, 68%) as an oil. IR (neat) 1636, 1254, 1082, 1026 cm^{-1}; ^{1}H NMR δ 5.56 (dd, 1H, J=11.2, 1.6 Hz), 5.41 (d, 1H, J=3.8 Hz), 4.05 (m, 5H), 3.88 (m, 1H), 2.05 (m, 1H), 1.86 (m, 1H), 1.61 (m, 1H), 1.26 (m, 61H), 1.12 (s, 3H), 1.01 (s, 3H); ^{13}C NMR δ 140.4 (d, J=226.6 Hz), 121.5 (d, J=20.8 Hz), 99.8 (d, J=9.2 Hz), 68.2, 62.4 (d, J=5.5 Hz), 49.1, 31.5, 31.3, 26.3, 24.9, 16.1 (d, J=6.0 Hz); ^{31}P NMR δ+9.32; HRMS calcd for $C_{13}H_{24}O_5P$ 291.1361; found 291.1352.

3.2.14. (±)-(4*R* *-Methyl-4a*R* *,6,7,8a*R* *-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-2-yl)-phosphonic acid dimethyl ester (6c). From 0.07 g (0.39 mmol) of **1a** and 180 μL (1.96 mmol) of 2,3 dihydro pyran was obtained after flash chromatography on silica gel (hexanes/ethyl acetate 1/3) **6c** (79 mg, 0.30 mmol, 77%) as an oil. IR (neat) 1634, 1453, 1258, 1089, 1046 cm^{-1}; ^{1}H NMR δ 5.51 (m, 1H), 5.25 (br s, 1H), 3.88 (ddd, 1H, J=11.3, 11.3, 3.5 Hz), 3.77 (dd, 3H, J=6.4, 0.6 Hz), 3.74 (dd, 3H, J=7.1, 0.6 Hz), 3.68 (m, 1H), 2.72 (m, 1H), 1.88 (m, 1H), 1.78–1.53 (m, 3H), 1.29 (m, 1H), 0.97 (d, 3H, J=7.4 Hz); ^{13}C NMR δ 141.3 (d, J=228.2 Hz), 119.4 (d, J=21.4 Hz), 97.9 (d, J=8.9 Hz), 61.1, 53.0, 36.4, 30.5 (d, J=13.8 Hz), 24.4, 17.6, 15.5; ^{31}P NMR δ +11.89; HRMS calcd for $C_{11}H_{18}O_5P$ 261.0891; found 261.0899.

3.2.15. [(2-*endo*,3-*exo*)-3-Methyl-bicyclo{2.2.1}hept-5-ene-2-carbonyl]-phosphonic acid diethyl ester 3. To a

1 M solution of 0.2 g (0.97 mmol, 1 equiv.) of **1** in CH_2Cl_2 at 0°C was added 0.22 mL (2.7 mmol, 2.8 equiv.) of freshly distilled cyclopentadiene. The reaction was allowed to warm at room temperature. After 17 h, the reaction mixture was concentrated in vacuo. The crude oil was purified by flash chromatography on silica gel eluting with hexanes/ethyl acetate (2/1) yielded 0.161 g of a mixture of **3** and of the corresponding carboxylic acid (5/1). **3**: IR (neat) 1726, 1688, 1253, 1020 cm^{-1}; ^1H NMR δ 6.22 (dd, 1H, $J=5.4$, 3.2 Hz), 5.81 (dd, 1H, $J=5.6$, 2.8 Hz), 4.20 (m, 4H), 3.44 (br s, 1H), 3.06 (m, 1H), 2.52 (m, 1H), 2.03 (m, 1H), 1.65 (m, 1H), 1.48 (m, 1H), 1.38 (m, 6H), 1.11 (d, 3H, $J=7.0$ Hz); ^{13}C NMR δ 21.07 (d, $J=162.2$ Hz), 138.7, 131.8, 63.4, 61.2 (d, $J=54.3$ Hz), 49.09 (d, $J=1.0$ Hz), 46.7, 46.2, 34.8 (d, $J=5.0$ Hz), 20.4, 16.2 (d, $J=5.7$ Hz); ^{31}P NMR δ −2.10, for the major isomer.

3.3. Tandem Diels–Alder reaction with [3,3] sigmatropic rearrangement

To 0.045 g (0.218 mmol) of **1** in 1.5 ml of CH_2Cl_2 at 0°C was added 0.05 mL (0.6 mmol, 2.8 equiv.) of freshly distilled cyclopentadiene. The reaction mixture was allowed to warm to room temperature. After 17 h, the reaction mixture was concentrated in vacuo (ratio **2/3** 1/8.8), the residue was diluted in 2 ml of CH_2Cl_2 and then cooled to −78°C. A 1 M solution of $SnCl_4$ in CH_2Cl_2 was added and after 1.5 h at −78°C. NMR analysis showed a **2/3** ratio of 7/1. The reaction mixture was worked up as usual. A purification on silica gel gave **2** as an oil (0.042 g, 0.154 mmol, 70%).

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