5.6 Hz, 1 H), 6.29 (dd, J = 5.1, 5.6 Hz, 1 H), 6.37 (d, J = 2.4 Hz, 1 H), 6.45–6.53 (m, 2 H); IR (KBr) 3050, 2950, 1724, 1348, 1210, 770 cm^{-1}; UV λ_{max} (EtOH) 230 (ϵ 1800, sh), 298 nm (180); MS (23 eV) m/z 184 (M^+, 30), 183 (100), 155 (20), 142 (20), 141 (95), 106 (30), 78 (63); HRMS calcd for $C_{13}H_{12}O$ 184.0887, found 184.0874.

Photochemical Transformation of 5a into 21. A solution of 9 mg of **5a** in 2 mL of methanol was deaerated by bubbling argon and irradiated with a high-pressure Hg lamp through Pyrex at 12 °C. After 20 min, GLC analysis (column A, 160 °C) showed the quantitative conversion of **5a** into a single product, which was obtained as a colorless solid after removal of the solvent and identified as **21**: mp 72–73 °C; ^1H NMR δ 2.38 (m, 1 H), 2.91–3.29 (m, 4 H), 3.44 (ddd, J = 1.0, 5.6, 5.9 Hz, 1 H), 6.09–6.23 (m, 3 H), 6.42 (ddd, J = 1.0, 5.9, 8.3 Hz, 1 H); ^{13}C NMR δ 33.6, 37.6, 39.5, 42.7, 44.0, 50.1, 58.8 (two signals overlap), 127.3, 128.3, 132.4, 139.9, 217.9; IR (film) 3050, 2970, 1755, 1378, 1298, 1260, 1212, 1026, 790, 760, 738, 716, 684 cm^{-1}; MS (23 eV) m/z 182 (M^+, 4), 181 (12), 154 (21), 153 (100), 152 (15), 128 (12), 104 (7); HRMS calcd for $C_{13}H_{10}O$ 182.0714, found 182.0712.

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Carbanion-Accelerated Claisen Rearrangements. 7. Phosphine Oxide and Phosphonate Anion Stabilizing Groups[1a]

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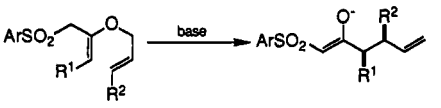
The utility of phosphine oxide and phosphonate groups has been examined in the context of the carbanion-accelerated Claisen rearrangement (CACR). Both of the groups permit the construction of substituted allyl vinyl ethers by allyl oxide addition to phosphorus-substituted allenes. Extensive optimization was required to suppress isomerization of both the allenes and the vinyl ethers. Using potassium dimsylate and lithium chloride as the base, both the phosphine oxides and phosphonates rearranged readily at room temperature with complete regioselectivity in good yield (62–93%). The phosphonates also showed a high level of diastereoselectivity (92% de). The characteristic features of the CACR were compared with the original arylsulfone version.

Introduction

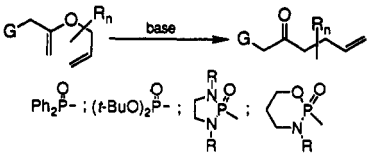
Recent reports from our laboratories[2] have documented the viability and synthetic potential of the carbanion-accelerated Claisen rearrangement (CACR) of allyl vinyl ethers (Scheme I). To date, these studies have focused on the use of the arylsulfonyl stabilizing group, and the results can be summarized as follows: (1) >300-fold rate acceleration over the thermal version, (2) complete regioselectivity, (3) high tolerance for substitution on the allyl vinyl ether (up to tetrasubstituted), (4) exclusive formation of trans olefins, and (5) high internal diastereoselectivity (90% de) for the syn or anti isomers.

To determine the effects of other anion stabilizing groups on rate and selectivity, we considered sulfoxides, sulfoximines, and sulfilimines, but found these sulfur-based groups problematic in preparation and rearrangement of the functionalized allyl vinyl ethers.[2] In contemplating alternative anion-stabilizing moieties, it became quickly apparent that the phosphorus-based groups offered a number of attractive advantages: (1) the ease of access to allenylphosphorus precursors,[3] (2) a well-established chemistry of phosphorus-stabilized allyl anions,[4] (3) potentially tunable reactivity in the choice of phosphorus derivative based on differences in pK_a (phosphine oxide, phosphonate, phosphonamidate, phosphonamide, et al.),[5] (4) the opportunity for manipulation of the keto phosphonate product,[6] and finally (5) the potential for chiral modification of the phosphorus to investigate auxiliary-based asymmetric induction.[7]

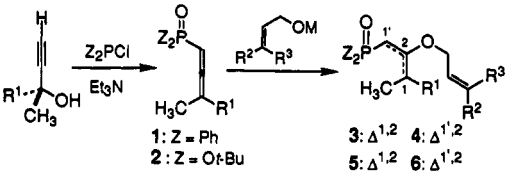
Scheme I



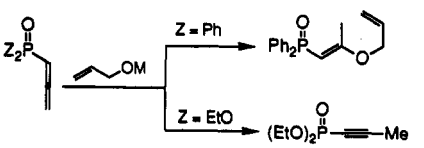
Scheme II



Scheme III



Scheme IV



(1) (a) Taken in part from Marlin, J. E. Ph.D. Thesis, University of Illinois, Urbana, IL, 1987. (b) Present Address: FJSRL/NC, USAF Academy, CO 80840.

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(4) Biellmann, J.-F.; Ducep, J.-B. *Org. React.* **1982**, *27*, 1.

(5) (a) The pK_a of diphenylbenzylphosphine oxide is 24 (DMSO). Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; Vol. 5A, p 359. (b) The pK_a of diethylbenzylphosphonate is 28 (DMSO). Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(6) Walker, B. J. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; Chapter 3.

0022-3263/91/1956-1003$02.50/0

Chart I

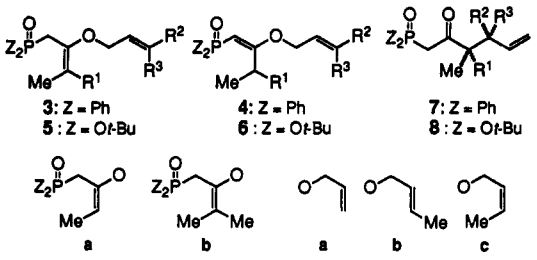


Table I. Preparation of Phosphorus Allenes

entry	Z	R^1	allene	yield, %
1	Ph	H	**1a**	76
2	Ph	Me	**1b**	72
3	*t*-BuO	H	**2a**	78
4	*t*-BuO	Me	**2b**	77

Our survey of phosphorus-based anion stabilizing groups encompassed the four types shown in Scheme II. In this paper we disclose in full our studies on the preparation and rearrangement of diphenylphosphine oxides and di-*tert*-butyl phosphonates. The rearrangements of the cyclic phosphonamides will be reported separately. The chiral phosphoramidates are the subject of an extensive study on the asymmetric induction in the CACR, the preliminary results of which have recently appeared.[8]

Results

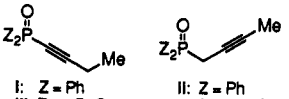
1. Preparation of the Allyl Vinyl Ethers. The construction of the requisite substrates for rearrangement follows exactly the protocol established in the arylsulfonyl series.[9] Thus, the allyl vinyl ethers **3** and **5** arise from addition of an allyl oxide to the appropriate phosphorus allenes (**1** and **2**), themselves easily available from propargylic alcohols (Scheme III). As in the case of the sulfones, the addition of allyl oxide is complicated by formation of the tautomeric allyl vinyl ethers **4** or **6**. Indeed, orienting experiments[2b] with the parent allenes showed either complete isomerization to the conjugated adduct or tautomerization of the allene[10a] (Scheme IV). Thus, to stabilize the allene and addition products against isomerization[10b] all substrates bear at least one methyl group at C(1).

Since most of the compounds studied herein arise from combination of similar subunits, a simplified numbering system is employed. Each structure is uniquely defined by the signature *N*xy where *N* = **3**, **4**, and **7** for the phosphine oxides and *N* = **5**, **6**, and **8** for the *tert*-butyl phosphonates (β,γ-unsaturated, α,β-unsaturated and rearrangement products, respectively). The substitution patterns are specified by x = a or b for R^1 and y = a-c for R^2 and R^3 according to the part structures (Chart I).

1.1. Synthesis of Allenes. Treatment of either 3-butyn-2-ol or 2-methyl-3-butyn-2-ol with a disubstituted chlorophosphine in the presence of triethylamine produced the unstable phosphite which underwent a facile Horner–Mark [2,3]-rearrangement[3] (Table I). In the phosphonate series **2**, di-*tert*-butyl phosphochloridate was prepared in situ and then treated with the propargyl alcohol. The *tert*-butyl ester was selected to suppress alcoholysis of the phosphonate in the next step. The room temperature production of the phosphorus allenes compared favorably to the corresponding sulfinate to sulfone rearrangement which requires refluxing CCl_4. The rearrangement products **1** and **2** displayed the characteristic allene stretching band in the infrared spectrum (1950–1970 cm^{-1}) in addition to the P=O absorption for phosphine oxides (1170–1190 cm^{-1}) and phosphonates (1250–1270 cm^{-1}).

1.2. Optimization of Allyloxide Additions. Although nucleophilic addition to phosphorus allenes is well known,[11] their enhanced tendency to undergo isomerization (vis a vis sulfonyl allenes) suggested that careful optimization of the reaction conditions would be necessary. Indeed, we have found that the nature of the phosphorus moiety is of primary importance in dictating the facility of addition (as well as secondary processes) in the expected reactivity order $Ph_2P(O) > (t\text{-}BuO)_2P(O) > (R_2N)_2P(O)$. Accordingly the phosphine oxides and phosphonates will be discussed separately.

1.2.1. Addition to Allenic Phosphine Oxides. In principle the additions of allylic alcohols are catalytic in base. In practice, the amount of base as well as the reaction time and temperature had a significant impact on the distribution of products. The optimized preparations are collected in Table II. As expected, extensive experimentation was required for the monosubstituted allenes. The first two entries show the sensitivity of structure to the stoichiometry of base. Additional optimization experiments showed that lower temperatures resulted in exclusive formation of acetylenic derivatives i and ii, while higher temperatures afforded only **4aa**. Using even less



base over a longer reaction time gave rise to a complex mixture of all of the above products. It is apparent that the course of the reaction depends on the relative nucleophilicity and the basicity of the allyl oxide. Acetylenes are formed at lower temperatures (less nucleophilic, more basic conditions) and the α,β-unsaturated isomer predominates at higher reaction temperatures or longer reaction times (more nucleophilic, less basic conditions). The β,γ-unsaturated derivatives are formed under reaction conditions between these extremes.

1.2.2. Addition to Allenic Phosphonates. The optimized preparations of allyl vinyl ethers in the phosphonate series are also shown in Table II. The desired β,γ-unsaturated products **5** could be obtained in good yields with a minimum of secondary product contamination. Thus, allyl and (*E*)- and (*Z*)-2-butenyl oxides could be

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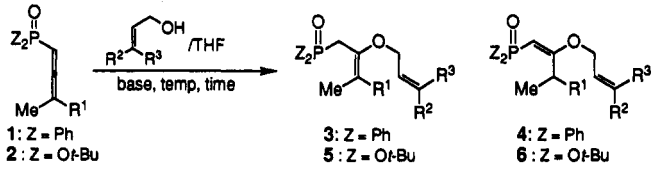
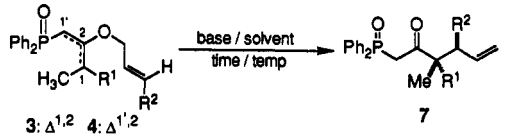
Table II. Allyloxide Additions to 1 and 2[a]



allene (conc)[b]	ROH, equiv	KH, equiv	time, h	temp, °C	product	Z	R^1	R^2	R^3	yield, %
1a (0.07)	2.0	0.50	0.5	−30	**3aa**	Ph	H	H	H	30
1a (0.21)	2.0	1.0	0.5	−30	**4aa**	Ph	H	H	H	58
1b (0.19)	1.5	0.22	3.5	0	**3ba**	Ph	Me	H	H	78
1b (0.10)	2.0	0.26	2.0	0	**3bb**	Ph	Me	Me	H	59
2a (0.11)	1.1	1.0	0.25	0	**5aa**	$(t\text{-BuO})_2$	H	H	H	70
2a (0.16)	1.1	1.0	0.25	0	**5ab**	$(t\text{-BuO})_2$	H	Me	H	65[c]
2a (0.11)	1.1	1.0	0.25	0	**5ac**	$(t\text{-BuO})_2$	H	H	Me	51[c]
2a (0.10)	1.1	1.0	0.25	20	**6ab**	$(t\text{-BuO})_2$	H	Me	H	56
2b (0.10)	1.1	1.0	2.5	0	**5ba**	$(t\text{-BuO})_2$	Me	H	H	61[d]
2b (0.10)	1.1	1.0	2.5	0	**5bb**	$(t\text{-BuO})_2$	Me	Me	H	59[e]

[a] All reactions run in THF. [b] Molarity. [c] The corresponding $\Delta^{1',2}$ isomer was isolated in trace amounts. [c] **8ba** was isolated in 7% yield. [e] **8bb** was isolated in 17% yield.

Table III. Rearrangements of Phosphine Oxides 3 and 4[a]



educt	KH, equiv	solvent	temp, °C	time, h	product	R^1	R^2	yield, %
3aa	2.1	DMSO	20	0.75	**7aa**	H	H	74
4aa	2.0	DMSO	20	0.75	**7aa**	H	H	32[b]
3ba	2.0	HMPA	20	0.25	**7ba**	Me	H	71
3bb	1.9	DMSO	20	0.25	**7bb**	Me	Me	91

[a] All reactions run at ca. 0.1 M. [b] Diphenyl(2-oxobutyl)phosphine oxide was isolated in 5% yield.

added to the monomethyl-substituted allenic phosphonate **2a** at 0 °C employing a full equivalent of potassium hydride. The additions occurred rapidly (15 min) and gave the desired products in acceptable yields. The α,β-unsaturated isomer **6ab** was readily prepared simply by raising the reaction temperature (20 °C). Allyl and 2-butenyl oxide additions to the dimethyl-substituted allene **2b** afforded the β,γ-unsaturated isomers **5ba** and **5bb** in good yield.

The conditions described for allyl oxide additions to allenic phosphonates were discovered only after extensive optimization. For example, addition in the presence of 0.23 equiv of base failed to go to completion, while addition at 20 °C with 0.40 equiv of potassium hydride gave predominantly a mixture of acetylenes iii and iv. The use of sodium hydride afforded only the unconjugated acetylene iv.

1.3. Structure of the Allyl Vinyl Ethers. The only structural ambiguity in the allyl vinyl ethers is the location and geometry of the vinyl ether double bond. The desired β,γ-unsaturated isomers displayed a characteristic absorption (phosphorus coupled) for the α-methylene protons. For **3** this resonance appeared at ca. 3.30 ppm ($^2J_{PH}$ = 14–16 Hz) and for **5** at ca. 2.65 ppm ($^2J_{PH}$ = 20–22 Hz). Furthermore, the infrared absorbance for the enol ether double bond was in the normal region (1670–1680 cm^{-1}). In all of these compounds only one isomer was ever detected. The vinyl ether double bond in **3** and **5** was assigned the *E* configuration by analogy to the stereochemical course of addition to other phosphorus allenes[11] and our previous studies with sulfonylallenes.[9] The consequences of steric approach control in allene additions have been discussed in detail.[11]

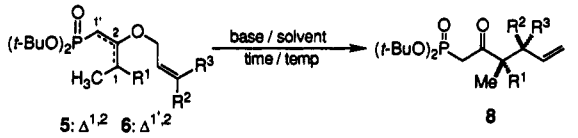
For the two α,β-unsaturated isomers the vinyl ether proton appeared as phosphorus-coupled doublet: **4aa**, 4.86 ppm ($^2J_{PH}$ = 4.9 Hz), and **6ab**, 4.48 ppm ($^2J_{PH}$ = 7.0 Hz). In these compounds the enol ether double bond resonance was shifted to lower energy by conjugation (1600–1620 cm^{-1}). Both **4aa** and **6ab** are formed as single isomers making stereochemical assignment difficult. Based on the anomalous downfield shift of the allylic methylene cis to the phosphorus moiety (**4aa**, 2.54 ppm; **6ab**, 2.57 ppm) the *E* configuration is assigned by analogy to the sulfone series.[9,12] Furthermore, this assignment is supported by an X-ray crystallographic structure determination of a related enol ether in the chiral phosphoramidate series.[8b]

Thus, a viable synthesis of the phosphorus-substituted allyl vinyl ethers was available. Importantly, the stereochemical control of the vinyl ether geometry in this reaction is assured. Homogeneous olefin geometry is critical for high internal and relative stereoselectivity in the subsequent rearrangement as described in the following section.

2. Anionic Rearrangements. 2.1. Phosphine Oxides. From consideration of the very similar pK_a values of benzyldiphenylphosphine oxide (24)[5a] and benzyl phenyl sulfone (23),[5b] we anticipated qualitatively similar rates of rearrangement. Thus for C(1) monosubstituted allyl vinyl ethers, reaction temperatures between 20 and 50 °C were expected. Based on extensive optimization in the sulfone series, potassium hydride was the base of choice in either DMSO or HMPA. It was, therefore, surprising to find these rearrangements complete in 15–45 min at 20

(12) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5863.

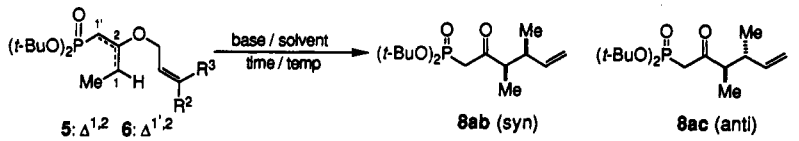
Table IV. Rearrangements of Phosphonates 5 and 6[a]



entry	educt	base (equiv)	LiCl equiv	solvent	temp, °C	time, h	product	R^1	R^2	R^3	yield, %
1	**5aa**	KH (1.9)	0	DMSO	20	0.25	**8aa**	H	H	H	46
2	**5aa**	KH (1.9)	3.2	DMSO	20	0.25	**8aa**	H	H	H	84
3	**5ab**	KH (2.3)	0	DMSO	20	0.25	**8ab**	H	Me	H	63[b]
4	**5ab**	KH (2.1)	5.1	DMSO	20	0.50	**8ab**	H	Me	H	93[c]
5	**5ac**	KH (1.5)	0	DMSO	20	0.75	**8ac**	H	H	Me	0[d]
6	**6ab**	KH (2.2)	5.9	DMSO	20	1.5	**8ac**	H	H	Me	79[c,e]
7	**5ba**	KH (1.8)	0	HMPA	20	0.25	**8ba**	Me	H	H	25[f]
8	**5ba**	KH (1.7)	5.4	DMSO	20	0.25	**8ba**	Me	H	H	85
9	**5ba**	KDA (1.9)	0	THF	−70→0	0.75	**8ba**	Me	H	H	63[g]
10	**5ba**	LDA (2.0)	0	THF	−70→20	0.50	**8ba**	Me	H	H	67[h]
11	**5bb**	KH (2.0)	0	DMSO	20	0.25	**8bb**	Me	Me	H	62
12	**5bb**	KH (1.8)	4.0	DMSO	20	0.25	**8bb**	Me	Me	H	92

[a] All reactions run at ca. 0.1 M. [b] Butanone v was isolated in 1% yield. [c] For diastereoselectivity, see Table V. [d] Butanone v was isolated in 76% yield. [e] Butanone v was isolated in 5% yield. [f] Furan **9** was isolated in 12% yield. [g] Allene **2** was isolated in 8% yield. [h] Allene **2** was isolated in 22% yield.

Table V. Internal Diastereoselectivity in the CACR[a]



educt	base	solvent	temp, °C	time, h	R^2	R^3	8ab/8ac[b]	yield, %
5ab	none	THF	100	10.0	Me	H	93:7	90
5ab	KH/LiCl	DMSO	20	0.25	Me	H	96:4	93
5ac	none	THF	100	8.0	H	Me	14:86	19
6ab	KH/LiCl	DMSO	20	1.5	Me	H	14:86	79

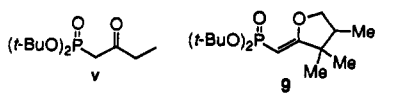
[a] All reactions run at ca. 0.1 M. [b] Ratios determined by integration of ^{31}P NMR spectra.

°C (Table III). The Claisen rearrangement products **7** were produced in good yield and with exclusive γ-regioselectivity. Only in the case of the α,β-unsaturated precursor **4aa** was the yield poor due to a competitive cleavage of the allyl ether. Although encouraged by the facility of rearrangement, the unacceptably poor yields of the allyl oxide addition to **1a** led us to concentrate efforts on the phosphonates.

2.2. Phosphonates. Because of the differences between sulfones and phosphonates, the first objective was to survey reaction conditions for the optimal base/solvent combination. The results of representative experiments and final optimized preparations are compiled in Table IV. Already in the rearrangements of the sulfones we noted the salutary effect of added lithium chloride on the yield of the Claisen products. Comparison of the entries 1 and 2, 3 and 4, 7 and 8, and 11 and 12 shows a significant increase in the yield of **8** accompanied by the elimination of side products when LiCl was used as additive. Under these conditions, the rearrangements proceeded at room temperature within 15 min in 85–93% yield. Even the α,β-unsaturated isomer **6ab** (entry 6) rearranged cleanly to give a single regioisomer as is now to be expected (the diastereoselectivity is discussed below). Although the rearrangement could be carried out in THF with soluble amide bases (entries 9 and 10), the yields were considerably lower and the allene **2** formed from β-elimination was isolated in significant amounts.

The only substrate which failed to undergo rearrangement was **5ac** bearing a (*Z*)-2-butenyloxy group. This was also observed in the sulfone series, but in contrast, added LiCl did not improve the results here. While the origin of the problem is not clear, this system is not well disposed to rearrangement as the thermolysis gave only 19% yield of the Claisen product (see Table V).

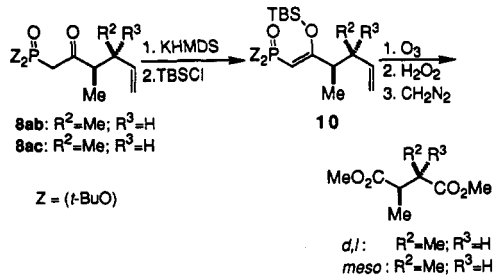
Some of the byproducts formed under other conditions provide interesting insights. The butanone v is related to the "cleavage" product observed in the sulfone series which stimulated the introduction of LiCl as an additive. In this case as well its formation is suppressed. A very unusual dihydrofuran product **9** was isolated from reaction of **5ba** in HMPA. The structure of this compound was deduced by spectroscopic analysis. The elemental composition was assured by mass spectrometry and the lack of an allyl double bond thus required a ring. The formulation of a five- rather than a six-membered ring follows from the presence of diastereotopic *gem*-dimethyl and methylene protons. The conjugated enol ether unit was indicated by the 1640-cm^{-1} absorbance in the IR spectrum.



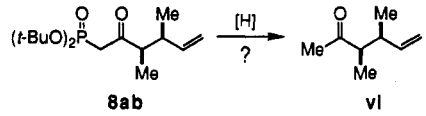
2.2.1. Internal Diastereoselectivity. An important feature of the aliphatic Claisen rearrangement and all of its variants is the high level of stereochemical coupling between olefin configuration and product stereochemistry.[13] The CACR has been shown to display equal or better selectivities in the rearrangement of allyl vinyl ethers monosubstituted at both C(1) and C(6).[2a,14] The results

(13) Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423.
(14) Denmark, S. E.; Harmata, M. A. *J. Org. Chem.* **1983**, *48*, 3369.

Scheme V



Scheme VI



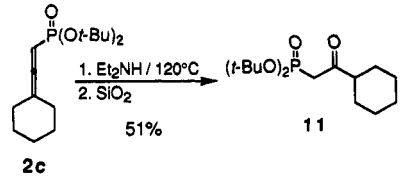
of CACR in the phosphorus series are collected in Table V. Three substrates were examined under both anionic (KH/DMSO/LiCl) and thermal reaction conditions. Thermal rearrangement (100 °C) of **5ab** derived from (*E*)-2-butenol (>99% *E*) proceeded cleanly to give the syn (**8ab**) and anti (**8ac**) keto phosphonates with high diastereoselectivity (see below for assignment). The formation of isomers was established by integration of the signals in the ^{31}P NMR spectrum. The carbanionic version also proceeded smoothly requiring only 15 min at room temperature and affording an excellent yield of the products with still higher stereoselectivity for the syn diastereomer.

As mentioned above, **5ac** bearing a (*Z*)-2-butenyloxy group (>99% *Z*) gave no products under anionic conditions, so a direct comparison of the chair/boat selectivity for **5ab** and **5ac** was not possible. Thermal rearrangement of **5ac** proceeded in only 19% yield and with a markedly eroded selectivity favoring the anti isomer, **8ac**. Remarkably, anionic rearrangement of the α,β-unsaturated allyl vinyl ether **6ab** bearing and (*E*)-2-butenyloxy group occurred rapidly and in good yield to afford an equivalent mixture of products (84:16) favoring the anti isomer! Clearly this must arise from permutation of the vinyl double bond in the anion compared to **5ab**. Moreover, a high barrier to anion rotation compared to rearrangement is required.

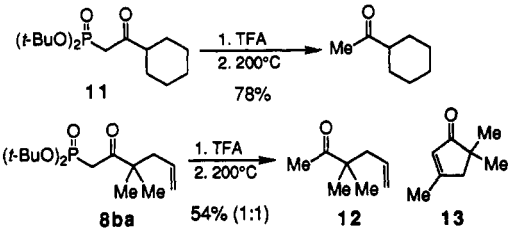
2.2.2. Configurational Assignment. Although the assignment of the diastereomers is well founded by analogy to other thermal and anionic Claisen rearrangements, the stereostructures of **8ab** and **8ac** were assured by degradation to the known dimethylsuccinic esters in Scheme V. The enolization of the keto phosphonate was initially problematic giving only 50% yield of the enol silane **10** with 1 equiv of KHMDS. For complete conversion, slightly more than 2 equiv of KHMDS were required. With excess of base it was essential to operate at −70 °C to avoid epimerization, presumable via the dianion. We suspect that the additional base is necessary to suppress internal return of the proton from HMDS upon silylation.[15] Ozonolysis of the crude silyl enol ether **10** followed by diazomethane esterification afforded the dimethyl dimethylsuccinates which were compared with authentic samples by capillary GC. Thus, a 92:8 mixture of **8ab**/**8ac** (^{31}P NMR δ **8ab**, 13.6 ppm; **8ac**, 13.4 ppm) produced a 92:8 mixture of *d,l*-/*meso*-dimethylsuccinic esters.

2.2.3. Cleavage of the C–P Bond. Since we had established the configuration of the 3,4-dimethyl-5-hexe-

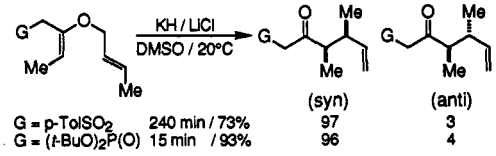
Scheme VII



Scheme VIII



Scheme IX



nones vi in the course of our earlier investigations, we initially envisioned a simpler degradation of **8ab** involving reductive dephosphorylation as formulated in Scheme VI. In contrast to the ready reductive cleavage of α-sulfonyl ketones,[16] this transformation was surprisingly difficult. To survey various methods, a simple substrate **11** was prepared by hydrolysis of the allenylphosphonate **2c** via the intermediate enamine[17] (Scheme VII).

All attempts to produce methyl cyclohexyl ketone by various reducing agents failed (Zn/AcOH,[18] Li naphthalenide,[19] Li/*n*-$PrNH_2$,[20] Li/$(CH_2NH_2)_2$[21]) either giving no identifiable products or carbonyl reduction to the hydroxy phosphonate. The *tert*-butyl ester groups in **11** could be removed with neat trifluoroacetic acid, but the resulting keto phosphonic acid was resistant to oxidation by lead tetraacetate.[22] The only successful cleavage of the P–C bond occurred upon pyrolysis (distillation) of the phosphonic acid to afford methyl cyclohexyl ketone in 78% yield (Scheme VIII). However, application of the deprotection/pyrolysis procedure to keto phosphonate **8ba** resulted in the production of a 1:1 mixture of the desired ketone **12** and the cyclopentenone **13** in 54% yield. Thus, the harsh, acidic conditions of this method are incompatible with the olefins present in all of these substrates. A similar incompatibility was anticipated for radical dephosphorylations[23] which were therefore not pursued.

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(16) (a) Johnson, C. R.; Kirchhoff, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 3602. (b) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

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(19) Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245.

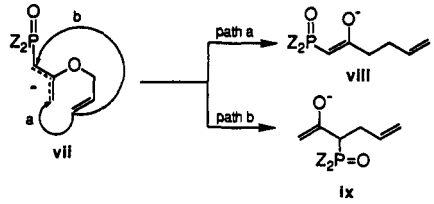
(20) Smith, M. B. In *Reduction*; Augustine, R. L., Ed.; Marcel Dekker: New York, 1968; Chapter 2.

(21) Reggel, L.; Friedel, R. A.; Wender, I. *J. Org. Chem.* **1957**, *22*, 891.

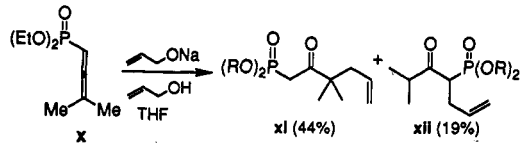
(22) Cordiero, M. L.; Pompliano, D. L.; Frost, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 332.

(23) (a) Crich, D.; Quintero, L. *Chem. Rev.* **1989**, *89*, 1413. (b) Barton, D. H. R.; Crich, D.; Kretzschmar, G. *J. Chem. Soc., Perkin Trans. 1* **1986**, 39. (c) Avila, L. Z.; Frost, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 8969.

Scheme X



Scheme XI



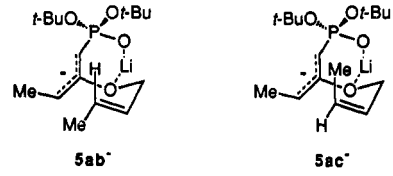
Discussion

Although accurate kinetic measurements have not been performed, the accelerating effect of phosphorus-based, anion-stabilizing groups in the Claisen rearrangement is qualitatively greater than for the corresponding sulfones. For the C(1) monomethyl family, all reactions occurred at room temperature (KH/DMSO) with the relative rate series: phosphonate > phosphine oxide > sulfone. The rate difference is more evident by comparison of the disubstituted allyl vinyl ether **5ab** with the corresponding sulfone (Scheme IX). While this is in line with the prediction based on pK_a's, such a simplistic picture is insufficient to explain the accelerating potential of a particular group. Clearly the detailed structure of the anion in addition to its thermodynamic basicity is significant. Extensive studies in these laboratories on the solution and solid state[24] as well as theoretical structures[25] of phosphorus-stabilized anions show that they are very different from sulfone-stabilized anions[26] in configuration and conformation. The consequences of anion structure are most significant in the asymmetric rearrangements employing chiral, phosphorus anion stabilizing groups.[8] However, it is interesting to note how these structural features may explain the difference between sulfur and phosphorus regarding internal diastereoselection (vide infra).

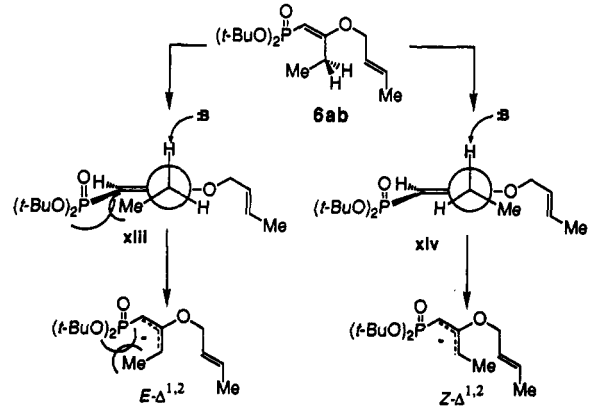
It is now well-established that the CACR gives exclusively one regioisomer independent of substitution pattern and anion-stabilizing group (Scheme X). The rationale provided in the sulfone series based on the large difference in pK_a for the two rearrangement products, holds equally well for phosphorus, as would an FMO rational based on HOMO coefficients in the anion.[25] Thus, under no circumstances with any substrate studied thus far have products ix derived from path b been observed.

However, in 1981, Cooper and Trippett[27] reported the production of, inter alia, the keto phosphonates xi and xii upon treatment of allene x with sodium allyloxide in ethanol (Scheme XI). They interpreted this result in terms of a carbanionic Claisen rearrangement with divergent pathways as illustrated in Scheme X. Our results (in dipolar aprotic solvents) do not allow this interpretation and we suggest that the Claisen products xi and xii arose by a thermal rearrangement of the tautomeric allyl vinyl ether formed under the equilibrating (protic) reaction conditions. Indeed we have isolated regioisomeric rearrangement products from certain substrates in the sulfone series but have subsequently found these to arise by a thermal process from α,β-unsaturated allyl vinyl ethers.[28] As we also detected rearrangement products in the allyloxide additions to **2b**, the product xi could have arisen from a CACR.

Chart II



Scheme XII



The high diastereoselectivity observed in the rearrangements of **5ab** is now expected in both thermal and anionic variants. Of particular note is the facility of the CACR. Disappointingly, the anti diastereomer **8ac** was not directly available by anionic rearrangement of the (*Z*)-2-butenyl educt **5ac**. The failure to observe rearrangement of this substrate may be due to the bulk of the *tert*-butyl phosphonate moiety. The reactive conformations of anions **5ab** and **5ac** are depicted in Chart II. Our NMR studies have revealed an extremely small barrier to rotation (<7 kcal/mol) about the P–C bond in anions.[24b] Thus, considering steric and chelation effects, the preferred orientation of the phosphonate places a bulky *tert*-butoxy group over the ring strongly disfavoring either the chair or boat transition structure compared to competing, nonproductive processes (i.e. fragmentation). Interestingly, the analogous sulfone structure only places an oxygen over the ring and in that series the compound corresponding to **5ac** rearranged cleanly, albeit slowly.

The striking similarity of the rearrangement selectivities for **5ac** (thermally) and **6ab** (anionically) is coincidence. In both cases, the anti isomer **8ac** was expected to predominate since one of the double bonds has inverted its geometry in each case. However, in the former case, 84/16 was lower than expected since the double bonds were of >99% homogeneity. The erosion in selectivity must arise from intervention of the boat transition state for reasons discussed above. It is reasonable to expect a bulky substituent of C(2) to destabilize the chair more than the boat transition structure in (*Z*)-2-butenyl ethers.

In the latter case, 84/16 was higher than expected based on the analogous sulfone which rearranged with 65/35, anti/syn selectivity.[2a] Once again, the greater bulk of the

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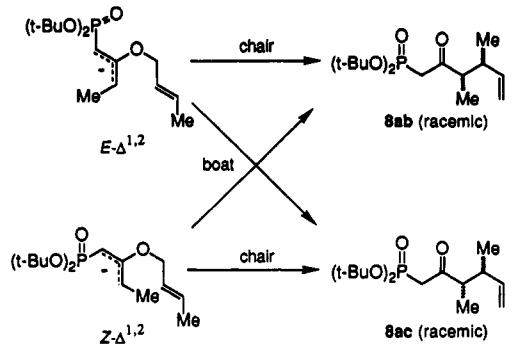
(25) Denmark, S. E.; Cramer, C. J. *J. Org. Chem.* **1990**, *55*, 1806.
(26) (a) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277. (b) Gais, J.-J.; Hellmann, G.; Lindner, H. J. *Ibid.* **1990**, *29*, 100 and references cited therein.
(27) Cooper, D.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2127.
(28) Sear, N. L., unpublished observations in the laboratories.

Scheme XIII



di-*tert*-butoxy phosphonate is responsible. Since the CACR of **5ab**, bearing an (*E*)-2-butenyloxy group, is highly syn selective, the anti selectivity in **6ab** *must* arise from permutation of the allyl anion geometry. The Newman projections depicted in Scheme XII show how two different allyl anions can arise by deprotonation of **6ab**. The (*E*)-$\Delta^{1,2}$ anion is similar to the species which is formed by deprotonation of **5ab** and is responsible for the highly selective formation of **8ab** therefrom. Formation of this anion from **6ab** must proceed via conformation xiii which experiences strong nonbonding interactions between the methyl and phosphonate groups as the carbon rehybridizes. However, deprotonation via conformation xiv avoids such interactions and leads to the isomeric (*Z*)-$\Delta^{1,2}$ anion (not accessible from **5ab**). Thus, the enhanced anti/syn selectivity observed in rearrangement of **6ab** compared to the analogous sulfone finds its origin in the greater deprotonation selectivity of the α,β-unsaturated precursors. Scheme XIII shows how anion geometry and transition-structure conformation are related. Clearly, the rotational barrier about C(1)–C(2) must be higher than the activation barrier for the rearrangement.[29] This analysis is supported by the results of rearrangements with chiral phosphorus groups wherein all permutations of anion geometry and chair–boat conformations lead to different isomers.[8c]

In view of the facility of C–X bond cleavage in α-heterosubstituted carbonyl compounds, we were surprised by the stability of **11** to reductive cleavage. Although C–P bonds are considered strong (60–65 kcal/mol),[30] their cleavage is well-known in the deactivation of homogeneous catalysts[31] and in the microbial metabolism of phosphonic acids.[32] The known chemical methods for cleavage (hydrolysis,[33a] photolysis,[33b] electrolysis,[33c] and hydride reduction[33d]) are of limited generality due to the unique substrate requirements. The failure of dissolving metal reducing agents may lie in the stability of the ketyl radical anion or in the reduction of the phosphonate with P–O bond cleavage. The pyrolytic process, albeit partially successful, is far too harsh for general use as seen in the formation of **13**. This compound may arise from an acid-catalyzed addition of the enol phosphonate to the olefin followed by loss of phosphorus acid. The radical dephosphorylations with lead tetraacetate[22] or with *n*-Bu_3SnH (with hydroxypyridinethiones)[23] were expected to lead to rapid ring closure.

Although we have recently documented a stereospecific C–P to C–N transform,[34] general reductive (to C–H) and constructive (to C–C) methods of C–P bond cleavage remain interesting challenges.

Conclusions

The carbanion-accelerated Claisen rearrangement has been extended to include phosphine oxides and phosphonates as anion-stabilizing groups. The preparative, stereochemical, and mechanistic features of this variant compare well with the original which employed the arylsulfonyl group. The preparation of allyl vinyl ethers by allyl oxide addition to phosphonyl allenes required considerable optimization, and the yields were generally lower than for sulfones. The rearrangements of both phosphine oxides **3** and phosphonates **5** were faster than the sulfones, and the yields were comparable. Potassium dimsylate with added LiCl was found to give the cleanest reactions. The level of internal diastereoselection was quite high, but (*Z*)-2-butenyl ethers were found to be incompatible. The resulting keto phosphonates were surprisingly resistant to reductive cleavage, though a pyrolytic dephosphorylation was demonstrated. The advantages of the phosphonate variant (rate of rearrangement, high internal stereoselection) have been parlayed with the versatile manipulation of configuration at phosphorus to produce an asymmetric anionic rearrangement. This study, together with the detailed solution and solid-state structural analysis of these phosphorus-stabilized anions will be reported in due course.

Experimental Section

General Methods. Bulb-to-bulb distillations were done on a Buchi GKR-50 Kugelrohr; boiling points (bp) refer to air bath temperatures and are uncorrected. Melting points (mp) were obtained in evacuated capillary tubes and are corrected. Analytical TLC was performed on 0.25 mm silica gel plates (Merck) with QF-254 indicator. Visualization was accomplished by UV light, iodine, and/or ethanolic solutions of sulfuric acid and vanillin. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: hexane ($CaCl_2$); ether ($CaSO_4/FeSO_4$); ethyl acetate (K_2CO_3). Reagent-grade benzene and acetone were used as received from commercial sources. All solvents used in reactions were freshly distilled from appropriate drying agents before use: THF (sodium benzophenone ketyl), hexane, HMPA, CH_2Cl_2, benzene, DMF, and DMSO all over CaH_2. All other reagents were recrystallized or distilled as necessary. Column (flash) chromatography was performed by the method of Still[35a] (32–63 μm silica gel, Woelm). Analytical gas chromatography was performed on a Varian 3700 chromatograph fitted with a flame-ionization detector (H_2 carrier gas, 2 mL/min) using an OV-17 capillary column (cOV-17, 39 m). *n*-Butyllithium was titrated by the double titration method of Gilman.[35b] Brine refers to a saturated aqueous solution of sodium chloride. All reactions were performed in oven- (125 °C) or flame-dried glassware under an inert atmosphere of dry N_2. The column used for analytical HPLC was 5 μm silica gel (250 × 4.6 mm). ^1H NMR spectra were recorded at 200, 300, or 360 MHz with tetramethylsilane (0.00 ppm) or chloroform (7.26 ppm) as an internal reference in $CDCl_3$ solutions. ^{13}C NMR spectra were recorded at 75.5 MHz with chloroform (77.0 ppm) as an internal reference in $CDCl_3$ solutions. ^{31}P NMR spectra were recorded at 121.4 MHz in acetone solutions with 85% phosphoric acid as an external reference. Chemical shifts are given in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet),

(29) The barrier to rotation about this bond in lithio phenyl allyl sulfone has been estimated to be >19.5 kcal/mol. Gais, H.-J.; Vollhardt, J.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 939.
(30) Hudson, R. F. *Pure Appl. Chem.* **1964**, *9*, 371.
(31) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.
(32) (a) Zeleznick, L. D.; Myers, T. C.; Tichner, E. B. *Biochem. Biophys. Acta* **1963**, *78*, 546. (b) Cook, A. M.; Daughton, C. G.; Alexander, M. *J. Bacteriol.* **1978**, *133*, 85.
(33) (a) Bestmann, H. J.; Schultz, H. *Chem. Ber.* **1962**, *95*, 2921. (b) Okamoto, Y.; Iwamoto, N.; Takamuku, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1516. (c) Bestmann, H. J.; Graf, G.; Kolewa, S.; Vilsmeier, E. *Chem. Ber.* **1970**, *103*, 2794. (d) Kondo, K.; Negishi, A.; Tunemoto, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 407.
(34) Denmark, S. E.; Dorow, R. L. *J. Org. Chem.* **1989**, *54*, 5.
(35) (a) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923. (b) Gilman, H.; Haubein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.

q (quadruplet), or m (multiplet). Coupling constants, J, are reported in hertz. Infrared spectra (IR) were obtained as neat liquids, or in $CHCl_3$ or CCl_4 solution. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67–100%), m (medium, 34–66%), w (weak, 0–33%), sh (shoulder), and br (broadened). Mass spectra (EI) were obtained with an ionization voltage of 10 or 70 eV. Data are reported in the form m/z (intensity relative to base = 100). High-resolution mass spectra were obtained on a Finnigan MAT 731 (EI) or VG-ZAB-HF (FAB) spectrometer. Elemental combustion analyses were performed by the University of Illinois Microanalytical Service Laboratory.

The following compounds were prepared by literature methods: (*Z*)-2-butenol,[9] (*E*)-2-butenol,[9] and diphenyl(3-methyl-1,2-butadienyl)phosphine oxide (**1b**).[36]

1,2-Butadienyldiphenylphosphine Oxide (1a). An oven-dried, 100-mL, 3-necked, round-bottomed flask equipped with a mechanical stirrer, dropping funnel, and thermometer was charged with 5.00 mL (27.8 mmol) of chlorodiphenylphosphine and 40 mL of Et_2O. The solution was cooled to 0 °C in an ice bath, and 3.20 mL (27.8 mmol) of triethylamine was added over 5 min. After the mixture was stirred for 15 min, 2.70 mL (27.9 mmol) of 3-butyn-2-ol in 20 mL of Et_2O was added via dropping funnel over 30 min. After being stirred at 0 °C for 45 min, the solution was warmed to room temperature and stirred overnight. The mixture was diluted with 100 mL water and extracted with Et_2O (3 × 100 mL). The Et_2O layers were washed with water and brine (1 × 75 mL each). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by recrystallization (hexane/ethyl acetate) to afford 5.35 g (75.5%) of **1a**. Data for **1a**: mp 88–89 °C; ^1H NMR (200 MHz) 7.84–7.68 (m, 4 H, aromatic H ortho to P=O), 7.65–7.36 (m, 6 H, aromatic), 5.82–5.73 (m, 1 H, HC(1)), 5.30–5.17 (m, 1 H, HC(3)), 1.62–1.53 (ddd, 3 H, J = 7.3, 6.6, 3.6, $H_3C(4)$); IR ($CHCl_3$) 3059 w, 2982 s, 2930 m (sh), 1951 s (C=C=C), 1591 w, 1485 w, 1439 s, 1367 s, 1310 w, 1170 s (P=O), 1120 s, 1101 m, 1067 w, 1025 w, 997 w, 857 m; MS (70 eV) 254 (M^+, 40), 202 (14), 201 (100), 77 (29), 51 (17); TLC R_f 0.25 (hexane/acetone, 1/1). Anal. Calcd for $C_{16}H_{15}OP$ (254.27): C, 75.58; H, 5.95; P, 12.18. Found: C, 75.46; H, 6.06; P, 12.42.

General Procedure for the Synthesis of Allenic Phosphonates. An oven-dried, 100-mL, 3-necked, round-bottomed flask equipped with a mechanical stirrer, dropping funnel, and thermometer was charged with 23.7 mmol of PCl_3 and 35 mL of dry benzene. The solution was cooled to 5 °C in an ice bath, and 71.1 mmol of triethylamine was added over 2 min. After the mixture was stirred for 20 min, a solution of 47.4 mmol of *tert*-butyl alcohol in 10 mL of benzene was added over 90 min. After the mixture was stirred for an additional 90 min, 23.7 mmol of the appropriate butynol in 10 mL of benzene was added dropwise over 10 min. The ice bath was removed, and the solution was stirred overnight at room temperature. The mixture was diluted with 50 mL of water and extracted with Et_2O (3 × 75 mL). The Et_2O layers were washed with 2 N HCl, 10% aqueous $NaHCO_3$, water, and brine (1 × 75 mL each). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation.

Di-*tert*-butyl 1,2-Butadienylphosphonate (2a). The crude product was distilled (Kugelrohr) to afford **2a** as a clear colorless oil (3.91 g, 78.3% yield). Data for **2a**: bp 90 °C (0.2 Torr); ^1H NMR (200 MHz) 5.38–5.23 (m, 2 H, HC(1), HC(3)), 1.81–1.67 (m, 3 H, $H_3C(4)$), 1.49 (s, 18 H, $(CH_3)_3C$); IR (CCl_4) 2982 s, 2932 m, 1958 m (C=C=C), 1721 w, 1476 m, 1395 m (sh), 1370 s, 1264 s (P=O), 1173 s, 1038 s (sh), 994 s, 918 m, 857 m, 830 m, 818 s; MS (70 eV) 135 (M^+ - 111, 14.1), 134 (65.4), 57 (100), 56 (10.8), 53 (10.3), 41 (38.3), 39 (11.3); high-resolution MS (FAB) calcd for $C_{12}H_{23}O_3P$ 247.1463, found 247.1467; TLC R_f 0.29 (hexane/acetone, 3/1).

Di-*tert*-butyl (3-Methyl-1,2-butadienyl)phosphonate (2b). The crude product was distilled (Kugelrohr) to afford 5.77 g (77.3%) of **2b** as a clear, colorless oil. Data for **2b**: bp 80 °C (0.05 Torr); ^1H NMR (200 MHz) 5.23–5.14 (m, 1 H, HC(1)), 1.75–1.69 (dd, 6 H, J = 7.3, 3.5, $(CH_3)_2C$) 1.47 (s, 18 H, $(CH_3)_3C$); IR (neat) 2985 s, 2940 s, 2880 m (sh), 2715 w, 1972 m (C=C=C), 1615 w, 1480 m, 1457 m, 1395 m, 1317 s, 1260 s (P=O), 1245 s (sh), 1171 s, 1040 s, 980 s (br), 922 s, 829 s, 798 s, 764 s, 696 s; MS (70 eV) 189 (M^+ - 71, 10.4), 149 (14.5), 148 (100), 147 (11.0), 84 (12.4), 67 (23.3), 66 (37.0), 57 (78.0), 41 (46.6), 39 (13.7); high-resoltuion MS calcd for $C_{13}H_{25}O_3P$ 260.1541, found 260.1547; TLC R_f 0.26 (hexane/acetone, 3/1).

Di-*tert*-butyl (2-Cyclohexylideneethenyl)phosphonate (2c). The crude product **2c** was obtained in 88.3% yield (15.2 g) and used without further purification. Data from **2c**: bp 130 °C (0.05 Torr); ^1H NMR (300 MHz) 5.21–5.17 (m, 1 H, HC(1)), 2.20–2.11 (m, 4 H, $H_2C(1')$, $H_2C(5')$), 1.65–1.37 (m, 6 H, $H_2C(2')$–$H_2C(4')$), 1.49 (s, 18 H, $(CH_3)_3C$); ^{13}C NMR (75.5 MHz) 206.0 (C(2)), 103.5 (C(3)), 83.5 (d, J = 204.5 Hz, C(1)), 82.0 (d, J = 8.3 Hz, $(CH_3)_3C$), 30.4 ($(CH_3)_3C$), 29.7 (C(1'), C(5')), 26.8 (C(2'), C(4')), 25.8 (C(3')); IR (neat) 2979 s, 2932 s, 2857 m (sh), 1960 m (C=C=C), 1467 m (sh), 1447 m, 1393 s, 1370 s, 1340 m, 1316 m, 1262 s (P=O), 1219 m (sh), 1173 s, 1038 s (sh), 980 s, 918 m, 837 m; MS (70 eV) 189 (M^+ - 111, 10.5), 188 (100), 198 (11), 107 (14), 106 (32), 91 (13), 57 (47), 43 (11), 41 (22); high-resolution MS calcd for $C_{16}H_{29}O_3P$ 300.1854, found 300.1851; TLC R_f 0.38 (hexane/acetone, 3/1).

General Procedure for the Synthesis of Allyl Vinyl Ethers. An oven-dried, 15-mL, 3-necked, round-bottomed flask equipped with stirring bar, septum, N_2 inlet, and thermometer was charged with KH dispersion (35% in oil). The KH dispersion was rinsed with hexane (3×) and suspended in 2.5 mL of THF. The suspension was cooled to 0 °C, and the allylic alcohol was added via syringe. After the mixture was stirred for 5 min, a solution of the allene (0.30 mmol) in 0.5 mL of THF was added via syringe. The reaction was monitored by TLC. Upon completion, the reaction was quenched with water and extracted with Et_2O (3 × 15 mL). The organic layers were washed with water and brine (1 × 15 mL each), dried over $MgSO_4$, filtered, and concentrated in vacuo.

(*E*)-Diphenyl[2-(2'-propenyloxy)-2-butenyl]phosphine Oxide (3aa). This addition was performed at −30 °C. The crude product was purified by column chromatography (hexane/acetone, 1/1) to afford 121 mg (29.8%) of **3aa**. An analytical sample was obtained by recrystallization from hexane/ethyl acetate. Data for **3aa**: mp 78–79 °C; ^1H NMR (200 MHz) 7.78–7.71 (m, 4 H, aromatic ortho H to P=O), 7.57–7.35 (m, 6 H, aromatic), 5.58–5.44 (m, 1 H, HC(2')), 5.09–4.94 (m, 2 H, $H_2C(3')$), 4.63–4.48 (m, 1 H, HC(3)), 3.90 (d, 2 H, J = 5.2, $H_2C(1')$), 3.28 (d, 2 H, J = 14.0, $H_2C(1)$), 1.63–1.50 (m, 3 H, $H_3C(4)$); IR (CCl_4) 3063 w, 2921 w, 1669 m, 1592 w, 1439 s, 1400 w, 1343 w, 1235 s, 1198 s (P=O), 1119 s, 1103 s, 999 w, 926 w; MS (70 eV) 312 (M^+, 2.50), 272 (10.5), 271 (60.9), 215 (19.6), 202 (31.3), 201 (88.1), 175 (10.2), 135 (15.0), 134 (64.6), 77 (21.5), 57 (100), 43 (21.7), 41 (51.0), 39 (16.8); high-resolution MS calcd for $C_{19}H_{21}O_2P$ 312.1279, found 312.1279; TLC R_f 0.38 (hexane/acetone, 1/1).

(*E*)-Diphenyl[2-(2'-propenyloxy)-1-butenyl]phosphine Oxide (4aa). This addition was performed at −30 °C. The crude product was purified by column chromatography (hexane/acetone, 1/1) to afford 373 mg (58.1%) of **4aa** as a white solid. An analytical sample was obtained by recrystallization from acetone/ethyl acetate. Data for **4aa**: mp 118–120 °C; ^1H NMR (360 MHz) 7.78–7.72 (m, 4 H, aromatic ortho H to P=O), 7.48–7.43 (m, 6 H, aromatic), 6.03–5.92 (m, 1 H, HC(2')), 5.37 (d, 1 H, J = 17.2, $H_tC(3')$), 5.30 (d, 1 H, J = 10.7, $H_cC(3')$), 4.86 (d, 1 H, J = 4.9, HC(1)), 4.36 (d, 2 H, J = 4.1, $H_2C(1')$), 2.54 (q, 2 H, J = 7.3, $H_2C(3)$), 0.99 (t, 3 H, J = 7.3, $H_3C(4)$); IR (CCl_4) 3061 w, 2976 w, 2939 w, 1599 s (C=C), 1462 w, 1437 m, 1377 w, 1343 m, 1304 w, 1188 s (P=O), 1116 s, 1093 s, 1069 w, 1028 w, 999 w, 928 m; MS (70 eV) 312 (M^+, 23.4), 311 (10.0), 283 (19.6), 270 (17.8), 255 (22.4), 244 (11.9), 243 (84.2), 241 (11.6), 228 (12.3), 215 (10.9), 203 (15.7), 202 (81.4), 201 (100), 199 (11.7), 183 (21.8), 165 (31.6), 155 (16.3), 125 (15.3), 97 (41.3), 91 (23.9), 78 (12.5), 77 (69.0), 51 (22.4), 47 (28.4), 44 (41.0), 43 (12.6), 41 (73.1), 39 (22.0), 32 (12.7); TLC R_f 0.38 (hexane/acetone, 1/1). Anal. Calcd for $C_{19}H_{21}O_2P$ (312.35): C, 73.06; H, 6.78; P, 9.92. Found: C, 72.77; H, 6.97; P, 9.81.

Diphenyl[3-methyl-2-(2'-propenyloxy)-2-butenyl]phosphine Oxide (3ba). Purification of the product by column chromatography (benzene/acetone, 2/1) afforded 1.96 g (78.2%) of **3ba**. Data for **3ba**: mp 65–67 °C; ^1H NMR (200 MHz) 7.83–7.74 (m, 4 H, aromatic H ortho to P=O), 7.58–7.41 (m, 6 H, aromatic), 5.84–5.70 (m, 1 H, HC(2')), 5.20–5.06 (m, 2 H, $H_2C(3')$), 4.05 (d,

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2 H, J = 5.0, $H_2C(1')$), 3.31 (d, 2 H, J = 15.5, $H_2C(1)$), 1.61 (d, 3 H, J = 5.1, $CH_3C(3)$), 1.35 (d, 3 H, J = 4.5, $CH_3C(3)$); IR ($CHCl_3$) 3082 w, 3065 w, 2990 s, 2922 m, 2863 w, 1678 w, 1487 w, 1440 s, 1200 w, 1381 w, 1310 w, 1260 m, 1177 s (P=O), 1138 s, 1120 s, 1100 s, 1086 s (sh), 1070 m, 1028 w, 995 m, 931 m, 836 w, 822 w; MS (70 eV) 326 (M^+, 3.74), 286 (12.7), 285 (70.3), 216 (11.6), 215 (22.7), 202 (22.2), 201 (100), 77 (22.7), 47 (10.3), 41 (17.3), 32 (15.2); TLC R_f 0.35 (hexane/acetone, 1/1). Anal. Calcd for $C_{20}H_{23}O_2P$ (326.38): C, 73.60; H, 7.10; P, 9.49. Found: C, 73.79; H, 6.85; P, 9.71.

Diphenyl[3-methyl-2-((*E*)-2′-butenyloxy)-2-butenyl]phosphine Oxide (3bb). Purification of the crude product by column chromatography (hexane/acetone, 1/1) afforded 375 mg (58.6%) of **3bb**. Data for **3bb**: mp 108–109 °C; ^1H NMR (200 MHz) 7.90–7.75 (m, 4 H, aromatic H ortho to P=O), 7.57–7.38 (m, 6 H, aromatic), 5.64–5.30 (m, 2 H, HC(2′), HC(3′)), 3.96 (d, 2 H, J = 6.2, $H_2C(1')$), 3.28 (d, 2 H, J = 15.6, $H_2C(1)$), 1.66 (d, 3 H, J = 6.2, $H_3C(4')$), 1.57 (d, 3 H, J = 5.2, $CH_3C(3)$), 1.32 (d, 3 H, J = 4.2, $CH_3C(3)$); IR (CCl_4) 3061 w, 2918 m, 2856 m, 1962 w, 1674 w, 1592 w, 1483 w, 1437 s, 1400 w, 1379 w, 1262 m, 1190 s (P=O), 1140 m, 1119 s, 1105 m, 1090 m, 1069 w, 1028 w, 999 m, 966 m, 904 w, 823 w; MS (70 eV) 340 (M^+, 6.62), 286 (34.5), 285 (48.9), 243 (13.9), 216 (29.4), 215 (58.5), 203 (11.2), 202 (82.5), 201 (100), 91 (11.2), 77 (32.5), 55 (32.6), 47 (17.7), 41 (16.9); TLC R_f 0.33 (hexane/acetone, 1/1). Anal. Calcd for $C_{21}H_{25}O_2P$ (340.41): C, 74.10; H, 7.40; P, 9.10. Found: C, 74.15; H, 7.64; P, 9.03.

(*E*)-Di-*tert*-butyl [2-(2′-Propenyloxy)-2-butenyl]phosphonate (5aa). The crude product was purified by column chromatography (hexane/acetone, 5/1) to afford 326 mg (69.5%) of **5aa**. Data for **5aa**: ^1H NMR (200 MHz) 6.04–5.87 (m, 1 H, HC(2′)), 5.32 (d, 1 H, J = 15.8, $H_tC(3')$), 5.18 (d, 1 H, J = 10.4, $H_cC(3')$), 4.56–4.46 (m, 1 H, HC(3)), 4.18 (d, 2 H, J = 5.4, $H_2C(1')$), 2.65 (d, 2 H, J = 21.3, $H_2C(1)$), 1.80–1.53 (m, 3 H, $H_3C(4)$), 1.49 (s, 18 H, $(CH_3)_3C$); IR (neat) 3081 w, 2979 s, 2933 m, 1669 m, 1648 w, 1636 w, 1617 m, 1477 w, 1457 w, 1426 w, 1393 m, 1369 s, 1346 m, 1304 w, 1266 s (P=O), 1210 m, 1175 s, 1141 m, 1102 s, 1039 s, 979 s, 918 m, 854 w; MS (70 eV) 304 (M^+, 1.05), 192 (34.7), 151 (81.5), 136 (21.8), 135 (15.0), 123 (24.6), 110 (35.9), 96 (16.4), 93 (17.9), 57 (59.8), 56 (12.2), 55 (13.3), 54 (10.7), 53 (10.6), 41 (100), 39 (22.6); high-resolution MS calcd for $C_{15}H_{29}O_4P$ 304.1825, found 304.1805; TLC R_f 0.34 (hexane/acetone, 3/1).

(*E*)-Di-*tert*-butyl [2-((*E*)-2′-Butenyloxy)-2-butenyl]phosphonate (5ab). Purification of the crude product by column chromatography (hexane/acetone, 5/1) afforded 395 mg (64.8%) of **5ab** together with less than 5% of **6ab**. Data for **5ab**: ^1H NMR (200 MHz) 5.73–5.62 (m, 2 H, HC(2′), HC(3′)), 4.54–4.48 (m, 1 H, HC(3)), 4.09 (d, 2 H, J = 4.8, $H_2C(1')$), 2.63 (d, 2 H, J = 20.6, $H_2C(1)$), 1.74–1.55 (m, 6 H, $H_3C(4)$, $H_3C(4')$), 1.48 (s, 18 H, $(CH_3)_3C$); IR (neat) 2979 s, 2930 m, 1667 m, 1616 w, 1456 w, 1392 m, 1368 s, 1346 w, 1267 s (P=O), 1211 m, 1175 m, 1140 m, 1103 s, 1038 s (sh), 980 s, 918 m, 853 w, 826 w; MS (70 eV) 152 (M^+ – 166, 100), 151 (32.4), 135 (26.9), 123 (24.8), 96 (27.8), 57 (44.1), 56 (11.3), 55 (42.8), 54 (13.5), 41 (39.8), 39 (17.3); high-resolution MS calcd for $C_{16}H_{31}O_4P$ 318.1960, found 318.1968; TLC R_f 0.32 (hexane/acetone, 3/1).

(*E*)-Di-*tert*-butyl [2-((*Z*)-2′-Butenyloxy)-2-butenyl]phosphonate (5ac). Purification of the crude product by column chromatography (hexane/acetone, 5/1) afforded 85 mg (50.9%) of **5ac**. Data for **5ac**: ^1H NMR (200 MHz) 5.65–5.58 (m, 2 H, HC(2′), HC(3′)), 4.56–4.50 (m, 1 H, HC(2)), 4.25 (d, 2 H, J = 4.1, $H_2C(1')$), 2.64 (d, 2 H, J = 21.3, $H_2C(1)$), 1.68–1.57 (m, 6 H, $H_3C(4)$, $H_3C(4')$), 1.49 (s, 18 H, $(CH_3)_3C$); IR (neat) 2980 s, 2930 m, 1669 m, 1617 w, 1478 w, 1393 m, 1370 s, 1348 w, 1267 s (P=O), 1211 m (sh), 1175 s, 1140 m, 1102 s, 1038 s (sh), 980 s, 918 m, 852 w, 826 w; MS (70 eV) 152 (M^+ – 166, 100), 151 (40.1), 135 (28.7), 123 (19.7), 96 (24.9), 57 (58.1), 56 (11.9), 55 (41.4), 54 (15.4), 53 (12.6), 41 (45.0), 39 (19.4); high-resolution MS calcd for $C_{16}H_{31}O_4P$ 318.1951, found 318.1955; TLC R_f 0.32 (hexane/acetone, 3/1).

Di-*tert*-butyl [2-((*E*)-2′-Butenyloxy)-1-butenyl]phosphonate (6ab). Purification of the crude product by column chromatography (hexane/acetone, 5/1) afforded 42 mg (56.4%) of **6ab**. Data for **6ab**: bp 115 °C (0.05 Torr); ^1H NMR (300 MHz) 5.82–5.72 (m, 1 H, HC(2′)), 5.65–5.58 (m, 1 H, HC(3′)), 4.48 (d, 1 H, J = 7.0, HC(1)), 4.16 (d, 2 H, J = 6.0, $H_2C(1')$), 2.57 (dq, 2 H, J = 7.5, 1.0, $H_2C(3)$), 1.73 (dd, 3 H, J = 5.3, 1.2, $H_3C(4')$), 1.49 (s, 18 H, $(CH_3)_3C$)), 1.11 (t, 3 H, J = 2.5, $H_3C(4)$); IR (neat) 2977 s, 2936 m, 1717 w, 1617 s (C=C), 1462 m, 1393 m, 1370 s, 1347 m, 1242 s (P=O), 1186 s, 1096 s, 1069 s, 1038 s, 972 s, 916 s, 828 m; MS (70 eV) 202 (M^+ – 116, 11.1), 201 (14.7), 177 (25.4), 152 (45.8), 149 (24.4), 135 (13.6), 133 (15.5), 131 (52.7), 123 (56.5), 107 (14.9), 105 (23.8), 104 (33.8), 103 (16.6), 91 (100), 78 (12.1), 77 (16.4), 65 (13.3), 57 (23.2), 55 (19.1), 51 (11.8), 41 (21.0), 40 (14.2), 32 (23.5); high-resolution MS (FAB) calcd for $C_{16}H_{31}O_4P$ 319.2038, found 319.2028; TLC R_f 0.32 (hexane/acetone, 3/1).

Di-*tert*-butyl [3-Methyl-2-(2′-propenyloxy)-2-butenyl]phosphonate (5ba). Purification of the crude product by column chromatography (hexane/acetone, 5/1) afforded 115 mg (60.7%) of **5ba**. Data for **5ba**: ^1H NMR (200 MHz) 6.07–5.88 (m, 1 H, HC(2′)), 5.33 (d, 1 H, J = 17.1, $H_tC(3')$), 5.16 (d, 1 H, J = 10.5, $H_cC(3')$), 4.22 (d, 2 H, J = 5.4, $H_2C(1')$), 2.66 (d, 2 H, J = 21.3, $H_2C(1)$), 1.72 (d, 3 H, J = 4.2, $CH_3C(3)$), 1.66 (d, 3 H, J = 3.0, $CH_3C(3)$), 1.50 (s, 18 H, $(CH_3)_3C$); IR (neat) 3080 w, 2980 s, 2930 s, 2875 m, 2720 w, 1679 m (C=C), 1647 w, 1479 m, 1455 m, 1423 m, 1393 m, 1368 s, 1262 s (P=O), 1249 s (sh), 1195 s, 1172 s, 1143 m, 1090 s, 1036 s, 975 s, 920 s, 846 w, 824 m, 778 m, 690 m, 665 m; MS (70 eV) 318 (M^+, 0.38), 206 (14.9), 165 (100), 107 (12.1), 96 (10.4), 83 (23.6), 41 (11.3); high-resolution MS calcd for $C_{16}H_{31}O_4P$ 318.1960, found 318.1960; TLC R_f 0.31 (hexane/acetone, 3/1).

Di-*tert*-Butyl [2-((*E*)-2′-Butenyloxy)-3-methyl-2-butenyl]phosphonate (5bb). Purification of the crude product by column chromatography (hexane/acetone, 5/1) afforded 269 mg (58.7%) of **5bb**. Data for **5bb**: ^1H NMR (200 MHz) 5.71–5.63 (m, 2 H, HC(2′), HC(3′)), 4.13 (d, 2 H, J = 5.4, $H_2C(1')$), 2.64 (d, 2 H, J = 21.6, $H_2C(1)$), 1.71–1.60 (m, 9 H, $(CH_3)_2C(3)$, $H_3C(4')$), 1.49 (s, 18 H, $(CH_3)_3C$); IR (neat) 2979 s, 2924 m, 1699 w, 1676 w, 1653 w, 1558 w, 1539 w, 1507 w, 1475 w, 1456 m, 1393 m, 1368 s, 1264 s (P=O), 1196 s, 1172 s, 1146 m (sh), 1096 s, 1038 s, 978 s, 918 m; MS (70 eV) 166 (M^+ – 166, 100), 165 (26.9), 149 (23.4), 123 (13.5), 96 (17.8), 71 (14.9), 68 (18.0), 57 (32.1), 55 (25.2), 41 (30.8); high-resolution MS calcd for $C_{17}H_{33}O_4P$ 332.2116, found 332.2115; TLC R_f 0.29 (hexane/acetone, 3/1).

General Procedure for the Carbanion-Accelerated Claisen Rearrangement in KH/HMPA/THF. An oven-dried, 3-necked, 15-mL, round-bottomed flask equipped with a stirring bar, septa, and a vacuum/N_2 inlet was charged with KH dispersion (35% in oil). The dispersion was rinsed with hexane (3×) and suspended in HMPA (2.5 mL). A solution of the allyl vinyl ether (0.30–0.33 mmol) in THF (0.75 mL) was added via syringe. The reaction was monitored by TLC. Upon completion, the reaction mixture was quenched with water (10 mL) and extracted with ether (3 × 15 mL). The organic layers were washed with water (3 × 15 mL) and brine (1 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo.

General Procedure for the Carbanion-Accelerated Claisen Rearrangement in KH/DMSO/THF. An oven-dried, 3-necked, 15-mL, round-bottomed flask equipped with a stirring bar, septa, and a vacuum/N_2 inlet was charged with KH dispersion (35% in oil). The dispersion was rinsed with hexane (3×), and DMSO (2.5 mL) was added. After stirring until H_2 evolution ceased (10 min), LiCl was added all at once (if necessary), followed by stirring for 10 more min. Then a solution of allyl vinyl ether (0.30–0.33 mmol) and THF (0.75 mL) was added via syringe. The reaction was monitored by TLC. Upon completion, the reaction mixture was quenched with water (10 mL) and extracted with ether (3 × 15 mL). The organic layers were washed with water (3 × 15 mL) and brine (1 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo.

General Procedure for the Carbanion-Accelerated Claisen Rearrangement in KDA/THF. An oven-dried, 15-mL, 3-necked, round-bottomed flask equipped with a septum, stirring bar, thermometer, and N_2 inlet was charged with KH dispersion (35% in oil). The dispersion was washed with hexane (3×) and suspended in THF (2 mL). The reaction mixture was cooled to 0 °C, and *tert*-butyl alcohol was added via syringe. The mixture was then cooled to −78 °C, and diisopropylamine was added. After 10 min, *n*-BuLi was added via syringe. After stirring for 10 more min, a solution of allyl vinyl ether (0.30–0.33 mmol) and 1 mL of THF was added via syringe. The solution was warmed to 0 °C and stirred until complete (by TLC). The reaction was quenched with water (10 mL) and extracted with Et_2O (3 × 15 mL). The organic layers were washed with water and brine (1

× 15 mL each). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo.

General Procedure for the Thermal Claisen Rearrangement. The allyl vinyl ether (0.10 mmol in THF) was placed in a high-pressure sealed vial and heated at the specified temperature until starting material was consumed (by TLC). The contents of the vial were transferred to a pear-shaped flask with Et_2O, and the solvent was removed in vacuo.

Diphenyl(3-methyl-2-oxo-5-hexenyl)phosphine Oxide (7aa). From **3aa**, KH/DMSO; column chromatography (hexane/acetone, 1/1) afforded 28 mg (74%) of **7aa**. From **4aa**, KH/DMSO; column chromatography (hexane/acetone, 1/1) afforded 40 mg (32%) of **7aa** along with 12 mg (5.4%) of diphenyl(2-oxobutyl)phosphine oxide. Data for **7aa**: mp 68–69 °C; ^{1}H NMR (200 MHz) 7.83–7.72 (m, 4 H, aromatic H ortho to P=O), 7.59–7.45 (m, 6 H, aromatic), 5.73–5.53 (m, 1 H, HC(5)), 5.04–4.99 (m, 2 H, $H_2C(6)$), 3.66 (d, 2 H, J = 15.2, $H_2C(1)$), 2.98–2.85 (m, 1 H, HC(3)), 2.40–1.98 (m, 2 H, $H_2C(4)$), 1.01 (d, 3 H, J = 6.7, $CH_3C(3)$); IR (CCl_4) 3081 w, 3063 w, 2979 w, 2911 w, 1709 s (C=O), 1456 w, 1439 m, 1208 s (P=O), 1121 m, 1107 w, 1028 w, 999 w, 918 w; MS (70 eV) 312 (M^+, 11.7), 243 (14.0), 216 (16.9), 215 (49.7), 202 (48.9), 201 (100), 111 (19.9), 91 (15.4), 77 (35.6), 51 (16.7), 47 (15.0), 41 (32.8), 39 (10.9); TLC R_f 0.44 (hexane/acetone, 1/1). Anal. Calcd for $C_{19}H_{21}O_2P$ (312.35): C, 73.06; H, 6.78; P, 9.92. Found: C, 73.07; H, 6.79; P, 9.98.

Diphenyl(3,3-dimethyl-2-oxo-5-hexenyl)phosphine Oxide (7ba). KH/HMPA/THF; column chromatography (benzene/acetone, 2/1) afforded 53 mg (71%) of **7ba**. KDA/THF; column chromatography (benzene/acetone, 2/1) afforded 68 mg (69.7%) of **7ba**. KH/DMSO; column chromatography (benzene/acetone, 2/1) afforded 63 mg (62.4%) of **7ba**. Data for **7ba**: mp 94–96 °C; ^{1}H NMR (200 MHz) 7.85–7.74 (m, 4 H, aromatic H ortho to P=O), 7.58–7.44 (m, 6 H, aromatic), 5.72–5.51 (m, 1 H, HC(5)), 5.04–4.96 (m, 2 H, $H_2C(6)$), 3.69 (d, 2 H, J = 15, $H_2C(1)$), 2.22 (d, 2 H, J = 7.0, $H_2C(4)$), 1.08 (s, 6 H, $(CH_3)_2C(3)$); IR (neat) 3060 w, 2980 s, 1915 m (sh), 2875 m (sh), 2483 w, 1705 s (C=O), 1640 w, 1591 w, 1485 w (sh), 1468 m, 1438 s, 1418 w (sh), 1388 m, 1366 m, 1330 w, 1305 w, 1205 s (P=O), 1119 s, 1105 m (sh), 1070 m, 1029 m, 997 s, 925 s, 850 m, 835 m, 750 s (br), 665 s, 625 w; MS (70 eV) 326 (M^+, 11.3), 243 (21.1), 216 (28.1), 215 (43.1), 202 (18.9), 201 (100), 77 (19.5), 55 (10.5), 47 (10.4), 41 (13.1); TLC R_f 0.42 (hexane/acetone, 1/1). Anal. Calcd for $C_{20}H_{23}O_2P$ (326.37): C, 73.60; H, 7.10; P, 9.49. Found: C, 73.51; H, 7.01; P, 9.53.

Diphenyl(3,3,4-trimethyl-2-oxo-5-hexenyl)phosphine Oxide (7bb). KH/DMSO; column chromatography (hexane/acetone, 1/1) afforded 95 mg (91%) of **7bb**. Data for **7bb**: mp 97.5–98.5 °C; ^{1}H NMR (360 MHz) 7.82–7.76 (m, 4 H, aromatic H ortho to P=O), 7.54–7.45 (m, 6 H, aromatic), 5.66–5.56 (m, 1 H, HC(5)), 5.02–4.97 (m, 2 H, $H_2C(6)$), 3.68 (d, 2 H, J = 14.7, $H_2C(1)$), 2.51–2.42 (m, 1 H, HC(3)), 1.02 (s, 3 H, $CH_3C(3)$), 1.01 (s, 3 H, $CH_3C(3)$), 0.86 (d, 3 H, J = 6.9, $CH_3C(4)$); IR (CCl_4) 3063 w, 2974 m, 1701 s (C=O), 1638 w, 1593 w, 1464 w, 1439 s, 1389 w, 1250 m, 1208 s (P=O), 1118 s, 1071 w, 1021 m, 997 m, 918 m, 847 w, 820 w, 816 s; MS (70 eV) 340 (M^+, 6.92), 286 (17.3), 285 (14.0), 243 (18.7), 216 (30.8), 215 (49.8), 202 (30.1), 201 (100), 77 (23.2), 55 (23.4), 41 (13.9); TLC R_f 0.41 (hexane/acetone, 1/1). Anal. Calcd for $C_{21}H_{25}O_2P$ (340.41): C, 74.10; H, 7.40; P, 9.10. Found: C, 74.05; H, 7.42; P, 9.20.

Di-*tert*-butyl (3-Methyl-2-oxo-5-hexenyl)phosphonate (8aa). KH/DMSO/LiCl; Kugelrohr distillation afforded 213 mg (84%) of **8aa**. Data for **8aa**: bp 125 °C (0.05 Torr); ^{1}H NMR (200 MHz) 5.74–5.66 (m, 1 H, HC(5)), 5.10–4.99 (m, 2 H, $H_2C(6)$), 3.02 (d, 2 H, J = 22.9, $H_2C(1)$), 2.99–2.86 (m, 1 H, HC(3)), 2.42–2.06 (m, 2 H, $H_2C(4)$), 1.50 (s, 18 H, $((CH_3)_3C)$, 1.08 (d, 3 H, J = 7.0, $CH_3C(3)$); IR (CCl_4) 2982 s, 2936 m, 1713 s (C=O), 1641 w, 1620 w, 1478 w, 1458 w, 1395 m, 1372 s, 1267 s (P=O), 1171 s, 1038 s (sh), 990 s, 918 m, 830 w, 818 s; MS (70 eV) 192 (M^+ – 112, 53.5), 179 (22.5), 175 (13.8), 123 (60.5), 110 (39.0), 96 (17.6), 95 (12.9), 93 (28.1), 69 (11.5), 57 (100), 56 (13.0), 43 (12.0), 41 (61.4), 39 (15.5); TLC R_f 0.29 (hexane/acetone, 1/1). Anal. Calcd for $C_{15}H_{29}O_4P$ (304.37): C, 59.19; H, 9.60; P, 10.18. Found: C, 58.89; H, 9.56; P, 10.44.

[*R*,*S*](3*l*,4*u*)-Di-*tert*-butyl (3,4-Dimethyl-2-oxo-5-hexenyl)phosphonate (8ab). KH/DMSO/LiCl; Kugelrohr distillation afforded 154 mg (93%) of **8ab**. KH/DMSO; column chromatography (hexane/acetone, 5/1) afforded 68 mg (62.5%) of **8ab** and 1 mg (1.0%) of di-*tert*-butyl (2-oxobutyl)phosphonate, v. Thermal; column chromatography (hexane/acetone, 5/1) afforded 100 mg (89.8%) of **8ab**. Data for **8ab**: bp 140 °C (0.03 Torr); ^{1}H NMR (200 MHz) 5.81–5.67 (m, 1 H, HC(5)), 5.02 (dt, 1 H, J = 5.4, 1.4, $H_tC(6)$), 4.95 (d, 1 H, J = 1.3, $H_cC(6)$), 3.20–2.81 (m, 3 H, $H_2C(1)$, HC(3)), 2.53–2.42 (m, 1 H, HC(4)), 1.50 (s, 18 H, $(CH_3)_3C$), 1.02 (d, 3 H, J = 6.7, $CH_3C(3)$), 0.95 (d, 3 H, J = 6.7, $CH_3(4)$); ^{31}P NMR (121.4 MHz) 13.6; IR (CCl_4) 3079 w, 2980 s, 2936 m, 1711 s (C=O), 1639 w, 1617 w, 1456 w (sh), 1395 m, 1370 s, 1267 s (P=O), 1171 s, 1038 s (sh), 984 s, 918 m, 876 w, 826 w; MS (70 eV) 206 (M^+ – 112, 15.9), 179 (14.1), 152 (18.8), 135 (25.5), 124 (60.1), 123 (49.7), 107 (12.1), 96 (15.7), 83 (11.3), 71 (10.7), 57 (100), 56 (16.5), 55 (35.6), 43 (10.2), 41 (58.9), 39 (19.6); TLC R_f 0.26 (hexane/acetone, 3/1). Anal. Calcd for $C_{16}H_{31}O_4P$ (318.40): C, 60.36; H, 9.81; P, 9.73. Found: C, 60.37; H, 9.72; P, 9.81.

[*R*,*S*](3*l*,4*l*)-Di-*tert*-butyl (3,4-Dimethyl-2-oxo-5-hexenyl)phosphonate (8ac). From **5ac**, thermal; column chromatography (hexane/acetone, 3/1) afforded 19 mg (19%) of **8ac**. From **6ab**, KH/LiCl/DMSO; column chromatography (hexane/acetone, 3/1) afforded 237 mg (79%) of **8ac** and 12 mg (5%) of v. Data for **8ac**: bp 140 °C (0.03 Torr); ^{1}H NMR (300 MHz) 5.70–5.59 (m, 1 H, HC(5)), 5.03–4.97 (m, 2 H, $H_2C(6)$), 3.14–2.90 (m, 2 H, $H_2C(1)$), 2.86–2.78 (m, 1 H, HC(3)), 2.51–2.46 (m, 1 H, HC(4)), 1.52 (s, 18 H, $(CH_3)_3C$), 1.03 (d, 3 H, J = 2.6, $CH_3C(3)$), 1.01 (s, 3 H, J = 2.4, $CH_3C(4)$); ^{31}P NMR (121.4 MHz) 13.4; IR (CCl_4) 3079 w, 2980 s, 2934 m, 2876 w (sh), 1711 s (C=O), 1642 w, 1617 w, 1478 w (sh), 1456 m, 1395 m, 1370 s, 1267 s (P=O), 1171 s, 1038 s, 992 s, 918 s, 876 w; MS (70 eV) 318 (M^+, 0.35), 206 (30.3), 189 (11.4), 179 (24.9), 152 (21.9), 135 (38.7), 134 (12.2), 125 (10.6), 124 (84.5), 123 (57.4), 107 (10.7), 96 (16.6), 83 (12.3), 71 (12.0), 57 (100), 56 (22.7), 55 (37.8), 53 (10.2), 43 (11.7), 41 (62.0), 39 (20.2); TLC R_f 0.26 (hexane/acetone, 3/1). Anal. Calcd for $C_{16}H_{31}O_4P$ (318.40): C, 60.36; H, 9.81; P, 9.73. Found: C, 60.26; H, 9.82; P, 9.65.

Di-*tert*-butyl (3,3-Dimethyl-2-oxo-5-hexenyl)phosphonate (8ba). KH/DMSO/LiCl; Kugelrohr distillation afforded 159 mg (85%) of **8ba**. KH/HMPA/THF; column chromatography (benzene/acetone, 2/1) afforded 36 mg (25%) of **8ba** and 17 mg (12%) of furan **9**. KDA/THF; Kugelrohr distillation afforded 32 mg (61%) of **8ba** and 4 mg (12%) of allene **2b**. LDA/THF; Kugelrohr distillation afforded 356 mg (67.2%) of **8ba** and 98 mg (22%) of allene **2b**. Data for **8ba**: bp 130 °C (0.05 Torr); ^{1}H NMR (300 MHz) 5.76–5.62 (m, 1 H, HC(5)), 5.06–5.00 (m, 2 H, $H_2C(6)$), 3.00 (d, 2 H, J = 22.8, $H_2C(1)$), 2.25 (d, 2 H, J = 7.4, $H_2C(4)$), 1.51 (s, 18 H, $(CH_3)_3C$), 1.15 (s, 6 H, $(CH_3)_2C$); IR (neat) 3076 w, 2979 s, 2936 m (sh), 1705 s (C=O), 1640 m, 1470 m, 1393 s, 1370 s, 1266 s (P=O), 1171 s, 1040 s, 982 s, 916 s, 868 w, 833 m; MS (10 eV) 318 (M^+, 0.79), 207 (10.7), 206 (73.7), 189 (21.6), 179 (100), 152 (17.9), 124 (10.2), 123 (68.9), 107 (31.9), 96 (40.7), 83 (19.1), 57 (54.1), 41 (10.5); TLC R_f 0.26 (hexane/acetone, 3/1). Anal. Calcd for $C_{16}H_{31}O_4P$ (318.40): C, 60.36; H, 9.81; P, 9.73. Found: C, 60.57; H, 9.65; P, 9.65. Data for **di-*tert*-butyl [(3′,3′,4′-trimethyl-2′-furanylidene)methyl]phosphonate (9)**: ^{1}H NMR (200 MHz) 4.41–4.33 (m, 2 H, HC(1), HC(5′)), 3.80 (t, 1 H, J = 8.9, HC(5′)), 2.11–2.00 (m, 1 H, HC(4′)), 1.48 (s, 18 H, $(CH_3)_3C$), 1.14 (s, 3 H, $CH_3C(3')$), 0.99 (s, 3 H, $CH_3C(3')$), 0.94 (d, 3 H, J = 7.0, $CH_3C(4')$); IR (CCl_4) 2975 s, 2932 m, 1640 s (C=C), 1460 m, 1391 s, 1368 s, 1337 m, 1277 m (sh), 1256 s (P=O), 1175 s, 1082 s, 1038 s, 997 s, 916 m, 866 m; MS (70 eV) 318 (M^+, 2.11), 207 (100), 206 (38.9), 191 (23.5), 189 (19.2), 164 (51.7), 125 (12.9), 124 (13.3), 123 (28.5), 111 (26.0), 107 (27.2), 69 (17.3), 67 (13.5), 57 (35.3), 56 (22.1), 55 (26.0), 43 (19.6), 41 (93.4), 39 (27.2); TLC R_f 0.38 (benzene/acetone, 2/1).

Di-*tert*-Butyl (3,3,4-Trimethyl-2-oxo-5-hexenyl)phosphonate (8bb). KH/DMSO/LiCl; Kugelrohr distillation afforded 97 mg (92%) of **8bb**. Data for **8bb**: bp 145 °C (0.05 Torr); ^{1}H NMR (300 MHz) 5.73–5.61 (m, 1 H, HC(5)), 5.05–5.00 (m, 2 H, $H_2C(6)$), 3.03 (d, 2 H, J = 22.6, $H_2C(1)$), 2.50–2.45 (m, 1 H, HC(4)), 1.52 (s, 18 H, $(CH_3)_3C$), 1.10 (s, 3 H, $CH_3C(3)$), 1.09 (s, 3 H, $CH_3C(3)$), 0.92 (d, 3 H, J = 4.9, $CH_3C(4)$); IR (CCl_4) 2979 s, 2936 s, 1707 s (C=O), 1637 w (sh), 1462 s, 1393 s, 1370 s, 1267 s (P=O), 1170 s, 1005 s, 918 s, 866 w, 834 m; MS (70 eV) 220 (M^+ – 112, 14.9), 179 (63.3), 166 (33.4), 165 (20.6), 152 (16.1), 149 (44.9), 139 (34.0), 123 (67.1), 99 (80.8), 97 (19.5), 96 (52.6), 73 (14.6), 57 (100), 56 (11.7), 55 (40.1), 41 (48.6), 39 (12.5); TLC R_f 0.25 (hexane/acetone, 3/1). Anal. Calcd for $C_{17}H_{33}O_4P$ (332.43): C,

61.42; H, 10.01; P, 9.32. Found: C, 61.46; H, 10.25; P, 9.11.

[*R*,*S*](3*l*,4*u*)-Di-*tert*-butyl [2-(*tert*-Butyldimethylsiloxy)-3,4-dimethyl-1,5-hexadienyl]phosphonate (10). An oven-dried, 5-mL, 2-necked, round-bottomed flask equipped with septum, stirring bar, and N_2 inlet was charged with 53.9 mg (0.17 mmol) of **8ab** and 1.5 mL of THF. The mixture was cooled to −78 °C. Potassium hexamethyldisilazide (1.07 mL of a 0.346 M solution in toluene, 0.37 mmol) was added via syringe. After 2 min, *tert*-butyldimethylsilyl chloride (64.5 mg, 0.43 mmol) in 300 μL of THF was added via syringe. After stirring for 30 min at −78 °C, the mixture was warmed to room temperature and transferred to a 15-mL centrifuge tube. Following centrifugation for 5 min at 5000 rpm, the supernatant liquid was decanted. The residue was washed with 3 mL of THF and resubjected to centrifugation (5 min at 5000 rpm). The supernatant liquids were combined, and the solvent was removed in vacuo to afford 70.3 mg (96%) of **10** which was used without further purification: ^{1}H NMR (300 MHz) 5.90–5.74 (m, 1 H, HC(5)), 4.94–4.81 (m, 2 H, H_2C(6)), 4.43 (d, 1 H, J = 8.0, HC(1)), 3.21–3.12 (m, 1 H, HC(3)), 2.27–2.16 (m, 1 H, HC(4)), 1.48 (s, 18 H, $(CH_3)_3CO$), 1.04 (d, 3 H, J = 6.8, H_3C(3)), 1.01 (d, 3 H, J = 6.8, H_3C(4)), 0.94 (s, 9 H, $(CH_3)_3CSi$), 0.19 (s, 6 H, $(CH_3)_2Si$).

[*R*,*S*](3*l*,4*u*)-Dimethyl 2,3-Dimethylsuccinate. An oven-dried, 15-mL, 3-necked, round-bottomed flask equipped with stirring bar, thermometer, and O_3 inlet and outlet tubes was charged with 3 mL of methyl acetate and cooled to −10 °C. A solution of **10** (67.3 mg, 0.16 mmol) in 1.5 mL of methyl acetate was added. Ozone was bubbled through the mixture until the blue color persisted. The mixture was then treated with 1.0 mL of 88% formic acid and 0.5 mL of 30% hydrogen peroxide. After warming to room temperature, this solution was stirred for 16 h. The solvents were removed in vacuo, and the crude product was dissolved in 3% NaOH and extracted with Et_2O (2 × 15 mL). The basic layer was acidified with 2 N H_2SO_4 and continuously extracted with Et_2O for 20 h. The organic layer was dried (Na_2SO_4), filtered, and concentrated in vacuo, and the residue was treated with an ethereal solution of diazomethane. Removal of solvent afforded 12.5 mg (46.1%) of dimethyl 2,3-dimethylsuccinate. GC analysis showed a syn to anti ratio of 92:8 (c-OV-17, 80 °C isothermal); t_R anti, 9.95 min; t_R syn, 11.14 min. The stereochemical assignments were made on the basis of coinjections with dimethyl 2,3-dimethylsuccinates obtained from authentic samples of the succinic acids (Aldrich).

Di-*tert*-butyl (2-Cyclohexyl-2-oxoethyl)phosphonate (11). A 250-mL, high-pressure vial equipped with a stirring bar was charged with 3.26 g (10.8 mmol) of allene **2c** and 25 mL of diethylamine. The mixture was heated at 120 °C for 16 h. The contents of the vial were transferred to a 100-mL pear-shaped flask with CH_2Cl_2, and the solvents were removed in vacuo. The crude enamine was hydrolyzed by column chromatography (hexane/acetone, 10/1) to yield 1.75 g (50.7%) of keto phosphonate **11**. Data for **11**: bp 120 °C (0.05 Torr); ^{1}H NMR (300 MHz) 3.00 (d, 2 H, J = 22.8, H_2C(1)), 2.70–2.62 (m, 1 H, HC(1′)), 1.85–1.14 (m, 10 H, H_2C(2′)–H_2C(6′)), 1.49 (s, 18 H, $(CH_3)_3C$); IR (neat) 2978 s, 2930 s, 2855 m, 1705 s (C=O), 1478 w, 1451 m, 1393 m, 1370 s, 1312 w, 1270 s (P=O), 1171 s, 1138 w, 1040 s (sh), 984 s, 920 m, 895 w, 860 w, 826 w; MS (70 eV) 207 (M^+ − 111, 14.5), 206 (100), 124 (28), 123 (36), 110 (14), 107 (31), 96 (16), 83 (14), 57 (66), 56 (10), 55 (19), 41 (37). Anal. Calcd for $C_{16}H_{31}O_4P$ (318.40): C, 60.36; H, 9.81; P, 9.73. Found: C, 60.23; H, 9.57; P, 9.54.

Thermal Dephosphorylation of Phosphonate (11). A flame-dried, 25-mL, round-bottomed flask equipped with a stirring bar and N_2 inlet was charged with 245 mg (0.769 mmol) of phosphonate **11** and 3 mL of CH_2Cl_2. Trifluoroacetic acid 35.5 μL (4.62 mmol) was added via syringe. After stirring for 30 min, the solvent was removed and the residue was distilled (air bath temperature 200 °C, 1 atm) to afford 76.0 mg (78.3%) of methyl cyclohexyl ketone. This material was identical by ^{1}H NMR to methyl cyclohexyl ketone purchased from Aldrich.

Thermal Dephosphorylation of Phosphonate (8ba). A flame-dried, 25-mL, round-bottomed flask equipped with a stirring bar and N_2 inlet was charged with 188 mg (0.590 mmol) of phosphonate **8ba** and 5 mL of CH_2Cl_2. Trifluoroacetic acid 275 μL (3.75 mmol) was added via syringe. After stirring for 30 min, the solvent was removed and the residue was distilled (air bath temperature 200 °C, 1 atm) to afford 40.2 mg (53.9%) of a 1:1 mixture of **12** and **13**.

Data from **12**: ^{1}H NMR (300 MHz) 5.75–5.56 (m, 1 H, HC(5)), 5.10–5.00 (m, 2 H, H_2C(6)), 2.27 (d, 2 H, J = 8.0, H_2C(4)), 2.17 (s, 3 H, H_3C(1)), 1.17 (s, 6 H, $(CH_3)_2C$(3)). Data from **13**: ^{1}H NMR (300 MHz) 5.56 (q, 1 H, J = 6.1, HC(2)), 2.18 (s, 2 H, H_2C(4)), 1.72 (d, 3 H, J = 6.1 Hz, CH_3C(3)), 1.21 (s, 6 H, $(CH_3)_2C$(5)).

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