$Mo(CO)_6$-Mediated Intramolecular Pauson−Khand Reaction of Substituted Diethyl 3-Allyloxy-1-Propynylphosphonates

Dorit Moradov,[†,‡] Abed Al Aziz Al Quntar,[†,§] Manar Youssef, Reem Smoum,[†] Abraham Rubinstein,[‡] and Morris Srebnik*[,†]

Department of Medicinal Chemistry and Natural Products and Department of Pharmaceutics, School of Pharmacy, Hebrew University in Jerusalem, Jerusalem 91120, Israel, and Department of Material Engineering, Faculty of Engineering, Al Quds University, Abu Dies, Jerusalem, Palestinian Authority

morris.srebnik@ekmd.huji.ac.il

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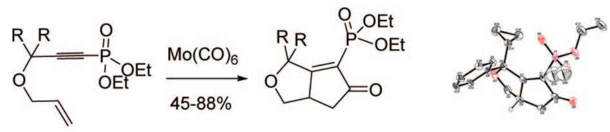

Cyclisation of diethyl 3-allyloxy-1-propynylphosphonates with $Mo(CO)_6$ under PK conditions to give 3-substituted-5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonate, **2a**−**h**, in 45−88% isolated yields was done. The R groups are always *syn* with H_b (where applicable). The stereochemistry was determined via both NMR and crystal X-ray analysis.

Introduction

Not only are vinylphosphonates important organic intermediates,[1−3] but we and others have shown that they possess considerable pharmacological activity.[4−6] In a series of papers, we have demonstrated that highly substituted vinylphosphonates can be prepared from 1-alkynylphosphonates and Zr(II) and Ti(II) reagents.[7−16] The Pauson−Khand reaction (PKR)[17−21] is compatible with many functional groups and enables the construction of relatively complex fused bicyclic structures. The use of phosphonate partners in the PKR has not been extensively explored. Thus, vinyl phosphonates using octacarbonyldicobalt have been reported to undergo intramolecular PKR to give selective formation of exocyclic 1,3-dienes versus PK cyclopentenone products depending on the reaction conditions.[22] Furthermore, Rivero and Carretero showed that under thermal conditions in acetonitrile there is mainly PK cyclopentenone product from the vinyl phosphonate starting material.[22] Kerr and co-workers have divulged that an intermolecular PKR using allylphosphonate led to two phosphorylated cyclopentenones products with moderate regioselectivity in the presence of DodSMe as promoter.[23]Having stated this, the same research team showed that modified PKR conditions with allylphosphonates in intermolecular processes led to elevated levels of regioselectivity between the two PK cyclopentenone products, hence establishing a normally less readily achieved regioselective intermolecular PK processes.[24] In contrast, the successful use of 1-alkynylphosphonates in the PK reaction has not been

† Department of Medicinal Chemistry and Natural Products, Hebrew University in Jerusalem.
‡ Department of Pharmaceutics, School of Pharmacy, Hebrew University in Jerusalem.
§ Department of Material Engineering, Faculty of Engineering, Al Quds University.

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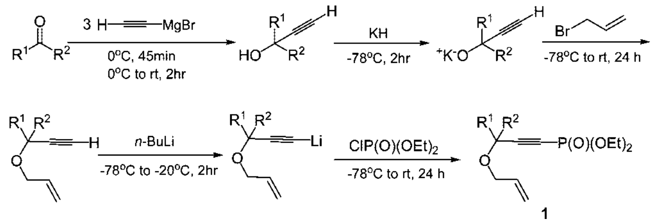
reported. However, in 1999, Spicer and co-workers reported the preparation of 1-alkynylphosphonate hexacarbonyldicobalt complexes.[25] Surprisingly, the authors found these complexes to be highly stable and totally inert to carbon−carbon bond formation. This was explained on the basis of the electron deficiency of the triple bond due to the electron-withdrawing character of the phosphonate group, which in turn deactivated the cobalt core of the complex preventing alkene coordination necessary for subsequent carbon−carbon bond formation according to the accepted mechanism of the PKR.[26] These observations intrigued us, and we reasoned that an intramolecular PKR should overcome the inertness of the 1-alkynylphosphonate cobalt complexes and lead to novel and interesting fused PK 2-phosphonocyclopentenones **2a−h**. Several approaches to monocyclic substituted 2-phosphonocyclopentenones have been reported in the literature. For instance, as byproduct in low yield from ϵ-*tert*-butyldimethylsilyloxy-α-diazo-β-ketophosphonates via a rhodium(II)-catalyzed C−H insertion reaction,[27−29] by ozonolysis/intramolecular aldol condensation of β-keto-ω-alkenylphosphonates requiring a multistep reaction,[30] from diethyl-2(5-methyl)furyl-hydroxymethylphosphonate via diethyl hex-3-en-2,5-dione-1-ylphosphonate followed by reduction and condensation,[31] by conversion of cyclic vinyl sulfones to vinylphosphonates,[32] and by Arbuzov reaction of cyclohexenylbromide (one example)[33] and as mixtures in low yield from enallenic phosphonates and α,β-unsaturated phosphoryl ketones with chromyl chloride.[34,35] This being the case, we decided to explore the possible use of 1-alkynylphosphonates in an intramolecular PKR, and in this paper, we describe our results for the general synthesis of the novel diethyl 3-substituted-5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonates **2** from diethyl 3-allyloxy-1-propynylphosphonates **1**. The preparation of **2** has not been previously reported.

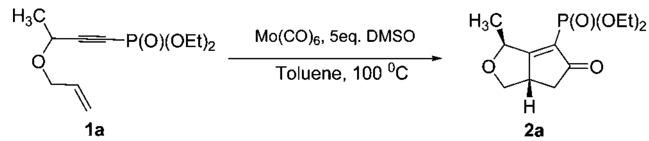
Results and Discussion

Synthesis of Diethyl 3-Allyloxy-1-propynylphosphonates 1. The diethyl 3-allyloxy-1-propynylphosphonates **1a−h** were synthesized by reacting allyl bromide with either the commercially available alkynyl alcohols (**1a−c**) or with alkynyl alcohols prepared by treatment of ethynylmagnesium bromide with aldehydes (**1d**,**e**) or ketones[36] (**1f−h**) as shown in Scheme 1.

SCHEME 1. Synthesis of Diethyl 3-Allyloxy-1-propynylphosphonates 1



SCHEME 2. Intramolecular PKR of 2a Mediated by $Mo(CO)_6$



After unsuccessful efforts to react alkynyl alcohols with allyl bromide using *n*-BuLi, we found that metalation with KH preceded smoothly.[37] The resultant 3-(allyloxy)-1-yne was lithiated with *n*-BuLi and phosphorylated with diethyl chlorophosphate to give yellowish oily products, diethyl 3-allyloxy-1-propynylphosphonates **1**, in 35−65% isolated yield after column chromatography (Table 1). The structures of **1** were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR. The hydrogens in the double-bond region ~5.2 and ~ 5.9 ppm, the double-bond carbons ~130 and ~120 ppm, together with the triple-bond carbons at ~100 and ~70 ppm coupled to phosphorus are consistent with structure **1**. Also, the peak at ~−6 ppm in the ^{31}P NMR is evidence that the phosphonate group coupled to sp-hybridized carbon.

Synthesis of Diethyl 3-Substituted 5-Oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonates 2. After the successful completion of the synthesis of the starting materials, diethyl 3-allyloxy-1-propynylphosphonates **1**, we started to explore the appropriate Pauson−Khand reaction (PKR) conditions in order to obtain the corresponding diethyl 3-substituted 5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonate **2**. Various conditions were initially tried and the results are summarized in Table 2.

Under conditions A or B, only ~50% of the diethyl 3-(allyloxy)but-1-ynylphosphonate, **1a**, reacted with octacarbonyldicobalt complex to form the alkynylphosphonate hexacarbonyldicobalt complex **1a′** (Figure 1), but **1a′** was extremely stable, and the Co complex did not further react by coordination to the double bond of the allyloxy group to form the desired diethyl 3-methyl-5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonate, **2a**, in agreement with the observations of Spicer et al.[25] The reaction could be followed by ^{31}P NMR in which the deep red color of alkynylphosphonate hexacarbonyldicobalt complex **1a′** has a chemical shift of ~20 ppm compared to **1a**, which has a chemical shift of ~−6 ppm.

When working under catalytic conditions C or D, the starting material **1a** was recovered and no traces of PK product **2a** were

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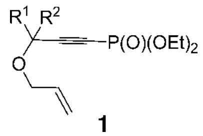
TABLE 1. Structures and Yields of Diethyl 3-Allyloxy-1-propynylphosphonates 1



1

entry	1	R^1	R^2	yield (%)
1	**1a**	H	methyl	56
2	**1b**	H	butyl	51
3	**1c**	H	pentyl	52
4	**1d**	H	nonyl	41
5	**1e**	H	phenyl	35
6	**1f**	pentamethylene		65
7	**1g**	hexamethylene		48
8	**1h**	cyclopropyl	phenyl	53

TABLE 2. Different Conditions for Intramolecular PKR of 1a

condition	metal	metal equiv	solvent	promoter	T (°C)	time (h)	**2a** (%)
A[a]	$Co_2(CO)_8$	1.3	CH_3CN		80	20	0
B[a]	$Co_2(CO)_8$	1.3	CH_2Cl_2	7 equiv of CH_3NO	25	1.5	0
C	$Co_2(CO)_8$	0.06	CH_3CN		80	48	0
D[b]	$Co_2(CO)_8$	0.05	THF	TMTU[c], CO balloon	70	6	0
E[d]	$Cr(CO)_6$	1.2	toluene	5 equiv of DMSO	100	24	0
F[d]	$Mo(CO)_6$	1.2	toluene	5 equiv of DMSO	100	2	78

[a] According to ref 22. [b] According to ref 38. [c] TMTU: tetramethylthiourea. [d] According to ref 39.

TABLE 3. Optimization of PKR of 1a under $Mo(CO)_6$

entry	solvent	T (°C)	time (h)	**2a** (%)
1	toluene	100	2	78
2	CH_3CN	82	8	69
3	DCE	83	24	0[a]
4	petroleum ether	50	24	0[a]
5	DMF	150	1	0[b]
6	THF	60	24	0[b]

[a] Starting material recovered. [b] Complex reaction mixture obtained.

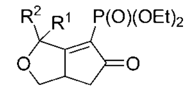
detected. Similar results were obtained when $Cr(CO)_6$ complex under conditions E was used, and only **1a** was detected in the reaction mixture. Interestingly, $Mo(CO)_6$, conditions F, gave the desired diethyl 3-methyl-5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonate product, **2a**, in 78% isolated yield and in a relatively short reaction time (Scheme 2).

We found that the reaction is solvent dependent, and the highest yield was obtained in toluene, though acetonitrile afforded satisfactory yields. In the case of dichloroethane (DCE) or petroleum ether, the diethyl 3-(allyloxy)but-1-propynylphosphonate **1a** remained intact, and no traces of **2a** were observed. On the other hand, when the reactions were carried out in DMF or THF, a mixture of many unidentified products was obtained as shown in Table 3.

The novel products 3-substituted 5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonates **2a–h** are stable and isolated by silica gel column chromatography in good yields (45–88%). Unlike **2f** and **2h**, which were obtained as yellowish solids, the other products are oils. The reaction was general for various R^1 and R^2 substituents including alkyl (**2a–d**), aryl (**2e**, **2h**), and cyclic (**2f**,**g**) as shown in Table 4. In certain cases, **2b–d**,**f**, in addition to the major PK product which has a chemical shift of ~10 ppm in ^{31}P NMR, a unidentified side product at ~7 ppm was observed in ~6% yield.

The structure and relative stereochemistry of product **2a** (Figure 2) was determined by NMR, GC/MS, and IR data. The

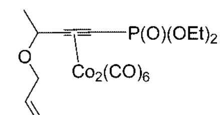
TABLE 4. Structures and Yields of 2 Obtained by PKR under Conditions F



2

entry	2	R^1	R^2	time (h)	conversion[a]/ isolated yield (%)[b]
1	**2a**	H	methyl	2	>98/78
2	**2b**	H	butyl	2	90/67
3	**2c**	H	pentyl	8	95/65
4	**2d**	H	nonyl	6	>98/58
5	**2e**	H	phenyl	5	96/45
6	**2f**	pentamethylene		4	97/81
7	**2g**	hexamethylene		3	>98/88
8	**2h**	phenyl	cyclopropyl	3	95/83

[a] Based on ^{31}P NMR. [b] After silica gel chromatography.



1a'

FIGURE 1. Structure of alkynylphosphonate hexacarbonyldicobalt complex **1a′**.

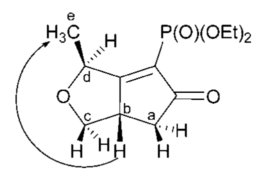


FIGURE 2. Structure and stereochemistry of **2a**.

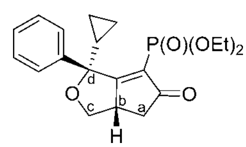


FIGURE 3. Structure of **2h**.

^{1}H NMR of the fused cyclopentenones showed that the two hydrogens on the same carbon (a or c) have different chemical shifts, which is indicative of diastereoisotopic hydrogens. Two-dimensional NMR including HSQC and NOESY techniques were essential to identify the structure and the stereochemistry of these compounds. The doublets in the regions ~125 ppm and ~198 ppm in ^{13}C NMR correspond to vinylic carbons split by phosphorus. Also, the doublet at ~204 ppm and the sharp peak at ~1700 cm^{-1} in IR are evidence of a carbonyl carbon. Concerning the stereochemistry determination, the NOESY NMR showed that there was an interaction between the hydrogen on carbon (b) and the hydrogens of the methyl group of **2a**, but no interaction was seen with the allylic hydrogen on carbon (d), which is indicative that the methyl group and the hydrogen on carbon (b) are *cis* and the two allylic hydrogens are *trans*.

Solving the stereochemistry of compound **2h** was more problematic (Figure 3). Protons H_b and H_c have the same chemical shift ~3.4 ppm (both on 300 and 500 MHz instruments). Thus, the relative stereochemistry of H_b and the phenyl or the cyclopropyl groups could not be determined from 2D NOESY NMR since both protons H_b and H_c show interactions with the phenyl and cyclopropyl groups.

In the absence of hydrogen on carbon (d), **2f−h**, two different chemical shifts for the OCH_2 carbons of the phosphonate ethoxy groups were seen at ~62.1 ppm and ~62.5 ppm in ^{13}C NMR. Initially we thought that this is due to hindered rotation around P−C bond. Interestingly, variable-temperature ^{13}C NMR for **2f** in DMSO-*d* from 25 to 130 °C did not show any coalescence of the OCH_2 groups, which is indicative that these carbons are diastereotopic rather than the result of hindered rotation around the P−C bond.

The stereochemistry of compound **2h** was determined by X-ray analysis. The phenyl group is *cis* to H_b, while the cyclopropyl group is in the *trans* position. In addition, there are several interesting aspects of the structure of **2h**. The dihedral angle (H14−C14−C6−O1) is 170.5° and therefore nearly bisects the plane of the cyclopropyl ring (C15−16). Also, the phenyl ring is essentially periplanar with the O1−C6 bond (O1−C6−C8−C13 = 7.43°), while O1 tilts toward the cyclopropyl group and imparts significant nonplanarity between the two fused five-membered rings (C1−C2−C4−C5 = 137.07°). The distances between O3/H14, O3/H9, and O1/H13 (2.320, 2.471, and 2.391 Å, respectively) rule out any intramolecular hydrogen bonding. In addition, it can be seen from the values of R_1 and wR_2 that the X-ray structure is of relatively poor quality. This result is probably a consequence of one of the ethoxy groups on the phosphorus which seems to be disordered. The crystal data and structure with the refinement are summarized in Table 5 and Figure 4.

Regarding the mechanism, the PKR proceeds by initial complexation to the triple bond.[19,20] Subsequently, complexation of the initially formed alkynyl complex with a C−C double bond is necessary. Co is a first-row transition metal. Mo is a second-row transition metal. Second-row d_p electrons are more basic and available than first row d_p electrons, and back-bonding is facilitated (i.e., CO stretching frequencies−$Co_2(CO)_8$, ν(CO) = 2044, $Mo(CO)_6$, ν(CO) = 2004). Thus, in the case of the Co complexes of **1**, the electron-withdrawing phosphonate group diminished the ability of Co to form alkene complexes. But, back-bonding of second- and third-row metal carbonyls is greater than for the first row, and Mo complexes of **1** could complex the alkene as illustrated in Scheme 3. DMSO facilitates the displacement of CO's.

Conclusion

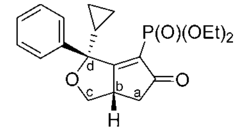
A facile synthesis of novel 3-substituted 5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonates **2a−h** starting from diethyl 3-allyloxy-1-propynylphosphonates **1a−h** utilizing PK conditions has been discussed. This reaction was successful using $Mo(CO)_6$, but with other metals like $Co_2(CO)_8$ and $Cr(CO)_6$ no traces of **2** were observed. The structure and the stereochemistry of the products and the reactants were confirmed by NMR, GC/MS, IR, X-ray and elemental analysis.

Experimental Section

Typical Procedure for the Synthesis of Diethyl 3-(Allyloxy)but-1-ynylphosphonate (1a). To KH (0.802 g, 20 mmol) suspended in dry THF (10 mL) was added 1-butyn-3-ol (1.402 g, 20 mmol) at −78 °C. After the mixture was stirred for 2 h at −78 °C, allyl bromide (2.419 g, 20 mmol) was added. The reaction mixture was gradually warmed to room temperature and was stirred overnight. Then the reaction mixture was quenched with 1 M HCl solution, the product was extracted with ether (3 × 50 mL), and the solvent was removed by rotavaporator after drying over Na_2SO_4.

Then, without further purification, 2.5 M *n*-BuLi (7.84 mL, 19.6 mmol) was added to the freshly prepared 3-(allyloxy)but-1-yne (2.156 g, 19.6 mmol) dissolved in dry ether (100 mL) at −78 °C. The reaction was gradually warmed to −20 °C and was stirred for

TABLE 5. Crystal and Structure Refinement for Compound 2h



2h

formula	$C_{20}H_{25}O_5P$
F_w	376.37
habit	plates
color	colorless
T, K	173(1)
radiation	Mo Kα
cryst size, mm	0.29 × 0.22 × 0.16
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	13.581(1)
b, Å	7.2664(6)
c, Å	20.337(2)
α, deg	90.00
β, deg	109.45
γ, deg	90.00
V, Å^3	1892.5(3)
Z	4
d_{calcd}, g cm^{-3}	1.321
F(000)	800
μ, mm^{-1}	0.173
θ range, deg	2.12−27.00
no. of unique reflns	20053
no. of restraints	0
hkl limits	−17, 17/−9, 9/−25, 25
no. of variables	227
no. of reflns with [$I > 2\sigma(I)$]	4122
final[a] R indices [$I > 2\sigma(I)$]	0.1301
wR_2	0.2867
R_1 indices (all data)	0.1359
wR_2	0.2903
max and min peak, e Å^{-3}	1.207 and −0.817
GOF	1.308

[a] $R1 = \Sigma||F_o| - |F_c||/|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$.

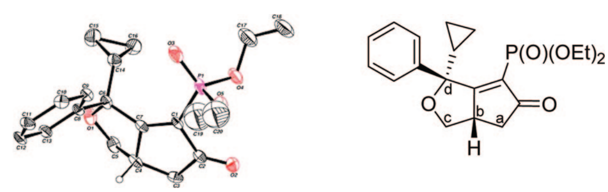
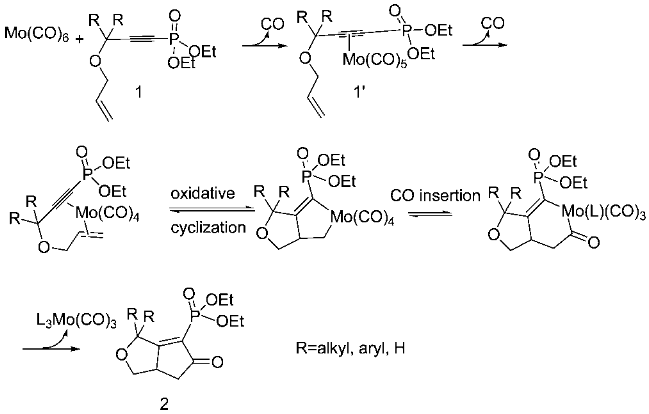


FIGURE 4. Molecular structure and stereochemistry of compound **2h**. View of the molecular structure of **2h** showing the atom-numbering scheme. Ellipsoid represents thermal displacement parameters at the 50% probability level. Selected bond distances (Å) and angles (deg) are as follows: C1−C7 = 1.337(6), C1−C2 = 1.495(7), C2−O2 = 1.210(6), C3−C4 = 1.517(7), C4−C7 = 1.506(6), C4−C5 = 1.507(7), C5−O1 = 1.435(7), C6−O1 = 1.451(5), C6−C7 = 1.505(7), C6−C14 = 1.519(7), C6−C8 = 1.539(6), O3−P1 = 1.454(4), O4−P1 = 1.565(4), O5−P1 = 1.557(5), C7−C1−C3 = 108.1(4), C1−C2−C3 = 107.7(4), C7−C4−C5 = 99.9(4), C7−C4−C3 = 104.2(4), C5−C4−C3 = 122.4(4), O1−C5−C4 = 105.2(4), O1−C6−C14 = 109.1(4), C7−C6−C14 = 114.1(4), O1−C6−C8 = 109.8(3), C14−C6−C8 = 111.1(4), C1−C7−C6 = 139.0(4), C4−C7−C6 = 107.0(4), C17−O4−P1 = 123.1(4), C19−O5−P1 = 118.3(7), O3−P1−O5 = 114.7(3), O3−P1−O4 = 115.9(3), O5−P1−O4 = 101.7(3), O3−P1−C1 = 116.8(2), O5−P1−C1 = 104.0(3), O4−P1−C1 = 101.7(2).

SCHEME 3. Proposed Mechanism for the Formation of 2 from 1 and $Mo(CO)_6$



2 h. Then the mixture was cooled to −78 °C, and diethyl chlorophosphate (3.382 g, 19.6 mmol) was added. Again, the mixture was gradually warmed to rt and stirred overnight. After the reaction was quenched by 1 M HCl, the product, diethyl 3-(allyloxy)but-1-ynylphosphonate (**1a**), was extracted with ether (3 × 50 mL). Then, after drying over Na_2SO_4, and removal of the solvents by rotavaporator, the product was separated by silica gel column chromatography using a gradient eluent of ethyl acetate/petroleum ether yielding 2.755 g (56%) of **1a**.

^{1}H NMR (300 MHz): δ 1.36 (t, 6H, J_{HH} = 7.2 Hz), 1.47 (d, 3H, J_{HH} = 6.9 Hz), 3.95 (dd, 1H, J_{HH} = 6.3 Hz, J_{HH} = 12.3 Hz), 4.08−4.21 (m, 5H), 4.27 (dd, 1H, J_{HH} = 3.3 Hz, J_{HH} = 6.6 Hz), 5.20 (d, 1H, J_{HH} = 10.5 Hz), 5.29 (d, 1H, J_{HH} = 16.8 Hz), 5.88 (m, 1H). ^{31}P NMR (121 MHz): δ −6.06. ^{13}C NMR (75.5 MHz): δ 133.50, 117.8, 99.9 (d, $^2J_{PC}$ = 48.7 Hz), 73.3 (d, $^1J_{PC}$ = 83.1 Hz), 69.9, 64.2 (d, $^3J_{PC}$ = 4.0 Hz), 63.0 (d, $^2J_{PC}$ = 5.4 Hz), 21.0, 15.9 (d, $^3J_{PC}$ = 6.9 Hz). Anal. Calcd for $C_{11}H_{19}O_4P$: C, 53.65; H, 7.78; P, 12.58. Found: C, 53.72; H, 7.61; P, 12.68.

Typical Procedure for the Synthesis of Diethyl 3-(Allyloxy)-dodec-1-ynylphosphonate (1d). To decanal (3.906 g, 25 mmol) in dry THF (100 mL) was added dropwise over 5 min under N_2 atmosphere 0.5 M ethynylmagnesium bromide in THF (150 mL, 75 mmol) at 0 °C. The reaction was stirred for 45 min at 0 °C, and then it was warmed to rt and stirred for an additional 2 h. After being cooled to 0 °C, the reaction was quenched with 1 M NH_4Cl solution. Then the product was extracted with ether (3 × 50 mL) and dried over Na_2SO_4, and the solvent was removed by rotavaporator.

Without further purification, to KH (0.562 g, 14 mmol) suspended in dry THF (7 mL) was added the freshly prepared dodec-1-yn-3-ol (2.548 g, 14 mmol) at −78 °C. After being stirred for 2 h at −78 °C, allyl bromide (1.694 g, 14 mmol) was added. The reaction mixture was gradually warmed to room temperature and was stirred overnight. Then the reaction mixture was quenched with 1 M HCl solution, the product was extracted with ether (3 × 50 mL), and the solvent was removed by rotavaporator after drying over Na_2SO_4.

Then, without further purification, 2.5 M *n*-BuLi (5.0 mL, 12.5 mmol) was added to the freshly prepared 3-(allyloxy)dodec-1-yne (2.775 g, 12.5 mmol) dissolved in dry ether (70 mL) at −78 °C. The reaction was gradually warmed to −20 °C and was stirred for 2 h. Then the mixture was cooled to −78 °C, and diethyl chlorophosphate (2.157 g, 12.5 mmol) was added. Again, the mixture was gradually warmed to rt and stirred overnight. After the reaction was quenched with 1 M HCl, the product, diethyl 3-(allyloxy)dodec-1-ynylphosphonate (**1d**), was extracted with ether (3 × 50 mL). Then, after drying over Na_2SO_4 and removal of the solvents by rotavaporator, the product was separated on silica gel column chromatography using a gradient eluent of ethyl acetate/petroleum ether to yield 3.670 g (41%) of **1d**.

^{1}H NMR (300 MHz): δ 0.87 (t, 3H, J_{HH} = 7.2 Hz), 1.20−1.32 (m, 12H), 1.36 (t, 6H, J_{HH} = 7.2 Hz), 1.41−1.50 (m, 2H), 1.71−1.86 (m, 2H), 3.95 (dd, 1H, J_{HH} = 6.3 Hz, J_{HH} = 12.6 Hz), 4.07−4.22 (m, 5H), 4.24 (m, 1H), 5.21 (d, 1H, J_{HH} = 10.5 Hz), 5.29 (d, 1H, J_{HH} = 15.6 Hz), 5.88 (m, 1H). ^{31}P NMR (121 MHz): δ −6.03. ^{13}C NMR (75.5 MHz): δ 133.9, 118.1, 99.9 (d, $^2J_{PC}$ = 48.7 Hz), 74.8, 74.3 (d, $^1J_{PC}$ = 85.1 Hz), 68.9 (d, $^3J_{PC}$ = 4.0 Hz), 63.4 (d, $^2J_{PC}$ = 5.4 Hz), 36.1, 32.0, 29.6, 29.6, 29.4, 29.4, 29.2, 22.8, 16.3 (d, $^3J_{PC}$ = 6.9 Hz), 14.3. Anal. Calcd for $C_{19}H_{35}O_4P$: C, 63.66; H, 9.84; P, 8.64. Found: C, 63.08; H, 9.45; P, 8.84.

Synthetic Procedure for Diethyl 3-Methyl-5-oxo-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-ylphosphonate (2a). To Mo-$(CO)_6$ (1.584 g, 6 mmol) in dry toluene (20 mL) was added diethyl 3-(allyloxy)but-1-ynylphosphonate, **1a** (1.230 g, 5 mmol), followed by addition of dry DMSO (1.952 g, 25 mmol). After being refluxed for 2 h at 100 °C, the reaction mixture was cooled, and ethyl acetate (20 mL) was added. The mixture was filtered through silica gel, and the product was separated on silica gel column chromatography using a gradient eluent of metanol/dichloromethane to yield 1.068 g (78%) of **2a**.

^{1}H NMR (300 MHz): δ 1.33 (t, 6H, J_{HH} = 6.9 Hz), 1.52 (d, 3H, J_{HH} = 6.6 Hz), 2.22 (dd, 1H, J_{HH} = 4.2 Hz, J_{HH} = 17.7 Hz), 2.7 (dd, 1H, J_{HH} = 6.6 Hz, J_{HH} =17.7 Hz), 3.29 (dd, 1H, J_{HH} = 7.5 Hz, J_{HH} = 11.1 Hz), 3.38 (m, 1H), 4.08−4.25 (m, 4H), 4.35 (t, 1H, J_{HH} = 7.5 Hz), 4.99 (q, 1H, J_{HH} = 6.6 Hz). ^{31}P NMR (121 MHz): δ 9.924. ^{13}C NMR (75.5 MHz): δ 204.7 (d, $^2J_{PC}$ = 13.7 Hz), 198.6 (d, $^2J_{PC}$ = 12.6 Hz), 125.8 (d, $^1J_{PC}$ = 194.9 Hz), 73.4, 70.7, 62.5 (d, $^2J_{PC}$ = 5.7 Hz), 44.9 (d, $^3J_{PC}$ = 15.4 Hz), 39.9 (d, $^3J_{PC}$ = 9.7 Hz), 19.7 (d, $^3J_{PC}$ = 1.1 Hz), 16.2 (d, $^3J_{PC}$ = 6.6 Hz). MS(EI): *m/z* 274 (15.8), 246 (11.5), 228 (46.7), 218 (16.5), 200 (100), 188 (19.7), 172 (21.6), 147 (14.1), 138 (11.5), 120 (13.4), 91 (18), 77 (21.8). Anal. Calcd for $C_{12}H_{19}O_5P$: C, 52.55; H, 6.98; P, 11.29. Found: C, 52.43; H, 7.05; P, 11.35.

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Supporting Information Available: ^{1}H and ^{13}C NMR for compounds **2a−h** and **1a−h**; details (CIF) of **2 h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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