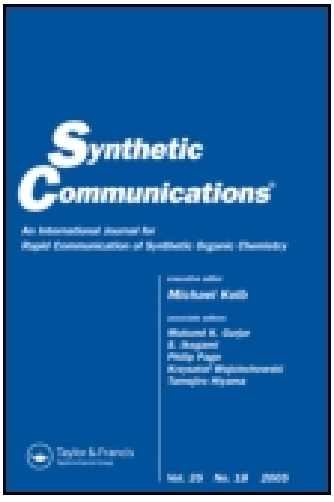
This article was downloaded by: [University of Washington Libraries]
On: 06 November 2014, At: 21:00
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Bifunctionalized Allenes, VII: Two Methods for One-Pot Synthesis of Sulfonyl-Functionalized Allenecarboxylates and Phosphorylated Allenes

Dr Valerij C. Christov [a] & Jordanka G. Ivanova [a]
[a] Department of Chemistry , University of Shumen , Shumen, Bulgaria
Published online: 16 Feb 2007.

To cite this article: Dr Valerij C. Christov & Jordanka G. Ivanova (2006) Bifunctionalized Allenes, VII: Two Methods for One-Pot Synthesis of Sulfonyl-Functionalized Allenecarboxylates and Phosphorylated Allenes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 36:15, 2231-2244, DOI: 10.1080/00397910600639042

To link to this article: http://dx.doi.org/10.1080/00397910600639042

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthetic Communications®, 36: 2231–2244, 2006
Copyright © Taylor & Francis Group, LLC
ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910600639042

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

Bifunctionalized Allenes, VII: Two Methods for One-Pot Synthesis of Sulfonyl-Functionalized Allenecarboxylates and Phosphorylated Allenes

Valerij C. Christov and Jordanka G. Ivanova
Department of Chemistry, University of Shumen, Shumen, Bulgaria

Abstract: Two new approaches to the synthesis of sulfonyl-functionalized allenecarboxylates and phosphorylated allenes are described. 2-Sulfonyl-alka-2,3-dienoates were readily prepared in an one-pot reaction by [2,3]-sigmatropic rearrangement of sulfinato-substituted 2-alkynoates, in situ generated from ethyl propynoate and subsequent treatment with lithium diisopropyl (LDA), ketone, trimethylchlorosilane (TMSCl), and the corresponding sulfinyl chlorides. Preparation of 1-sulfonyl-alka-1,2-dienephosphonates and -1,2-dienyl phosphine oxides consists of the reaction of the lithio compounds, in situ generated from phosphorylated allenes and LDA, with the corresponding sulfonyl chlorides.

Keywords: [2,3]-Sigmatropic rearrangement, 1-sulfonyl-alka-1,2-dienephosphonates, 1-sulfonyl-alka-1,2-dienyl phosphine oxides, 2-sulfonyl-alka-2,3-dienoates, synthesis

Allenes are attractive starting points for synthesis, in large part because of the high reactivity engendered by strain. In the past three decades, synthesis and use[1] of allene derivatives have been expanded in preparative organic chemistry.[2] An impressive number of heterocyclic systems has been prepared from allenic starting materials. The electrophilic cyclization[3] of a variety of monofunctionalized allenes such as alcohols,[4] carboxylic acids and their esters,[5] sulfoxides,[6a] sulfinates,[6b] sulfones,[6b–d] phosphonates,[7] phosphinates,[7] and phosphine oxides[6] to heterocyclic systems has received

Received in the UK October 7, 2005
Address correspondence to Dr. Valerij C. Christov, Department of Chemistry, University of Shumen, 115, Universitetska str., Shumen BG-9700, Bulgaria. Fax: +359-54-830 371; E-mail: vchristo@shu-bg.net

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

considerable attention because of its synthetic utility and remarkable stereoselectivity.[3d,4,5b,5f,6c,6d,7]

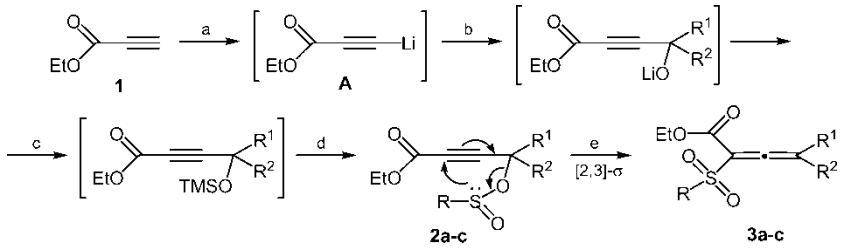
Reaction of propargyl alcohols with halogen-containing reagents such as sulfenyl halides[8] and sulfinyl chlorides[9] is a convenient method for preparation of propargyl compounds (sulfenates or sulfinates), which usually undergo [2,3]-sigmatropic rearangement to allenic products[8–11] (sulfoxides or sulfones). Synthesis of alkyl 2,3-alkadienoates by the Wittig reaction[12] and by other methods have been reviewed.[13] The synthesis of α-thioallenecarboxylates by metallation of an allene sulfide, followed by treatment with methyl chloroformate, was mentioned by H. G. Viehe[14a] without the experimental datails. An alternative route that enables the preparation of thio-,[14b] sulfinyl-,[14b,14c] and sulfonyl-substituted[14b] allenecarboxylates starts from methyl 4-hydroxy-2-alkynoate.

On the other hand, a most important aspect for applications of 1-acceptor-substituted allenes is the relatively high acidity of the hydrogen atom at C-1 atom, for examples, 1-alkoxyallenes,[15] α-allenic esters,[16] 1-allenyl sulfide,[17a] sulfoxides,[17b] sulfineamides,[17c] and sulfone.[17d] The literature data show that the proton at the C-1 atom from the allenic system is easy displaceable with different electrophilic reagents. For example, α-metallation of an allenyl phosphine oxide (introduction of deuterium in the α-position) has been observed.[18a] Application of allenic phosphonates to the synthesis of structurally interesting molecules was made by R. S. Macomber,[18b–d] as shown in the construction of bicyclic cumulatriene as an elegant example.[18e]

As a part of our research program on the chemistry of the heteroatom-functionalized polyenes, we required convenient methods to introduce sulfonyl and phosphoryl groups in the α-position to the ester group of allenecarboxylates. The previously mentioned groups attract increasing attention as useful functionalities in organic synthesis. Of particular interest are the applications of these groups as temporary transformers of chemical reactivity of the allenic system in the synthesis of eventually heterocyclic compounds.

In a continuation of our previous reports on the synthesis[19a,19b] and electrophile-induced cyclization reactions[19c–f] of bifunctionalized allenes, we have found two efficient methods for synthesis of 2-sulfonyl-alka-2,3-dienoates as well as 1-sulfonyl-alka-1,2-dienephosphonates and 1,2-dienyl phosphine oxides.

The first method for one-pot preparation[19b] of ethyl 2-sulfonyl-allenecarboxylates **3a–c** consists of the following cascade steps. Reaction of the lithio compounds **A**, generated in situ from ethyl propynoate **1** and LDA, with acetone or cyclohexanone and subsequent treatment with TMSCl and after that with methane- or trichloromethanesulfinyl chloride, gives ethoxycarbonyl-substituted propargyl sulfinates **2a–c**. These are surprisingly stable and were isolated in 70–73% yield. Reflux of sulfinates **2a–c** (which may be or not be isolated) in toluene provokes a [2,3]-sigmatropic rearangement to the expected 2-sulfonyl-2,3-alkadienoates **3a–c**, according to the reaction sequence outlined in Scheme 1 and Table 1.



Scheme 1. Synthesis of 2-sulfonyl-substituted allenecarboxylates. Reagents and conditions: a) LDA, THF, −100°C, 1 h; b) $R^1R^2C{=}O$ [$R^1 = R^2 = Me$, $R^1 + R^2 = -(CH_2)_5-$], THF, −100°C, 10 min; c) TMSCl, THF, −100 to −10°C, 10 min; d) RS(O)Cl (R = Me, CCl_3), THF, −10°C to rt, 1 h; e) toluene, reflux, 3 h.

The starting materials in the synthesis of 1-sulfonyl-functionalized alka-1,2-dienephosphonates **6a–f** and 1,2-dienyl phosphine oxides **7a–d** are the phosphorylated allenes **5a–d**. They are readily available by the reaction[20] of the appropriate alkynols **4a, b** with diethyl chlorophosphite or diphenyl chlorophosphine in the presence of triethyl amine. In this case, in situ generated alkynyl derivatives **B** cannot be isolated but rather undergo spontaneous [2,3]-sigmatropic rearrangement in the presence of 3 mol% hydrochloric acid to the desired allenephosphonates or allenyl phosphine oxides **5a–d** (Scheme 2, Table 2).

We found that the phosphorylated allenes **5a–d** can smoothly be deprotonated at the α-position by LDA in THF under an argon atmosphere. The in situ resulting lithio compounds **C** can react with methane-, trichloromethane-, or trimethylsilyloxy-sulfonyl chlorides, leading to 1-sulfonyl-substituted allenephosphonates **6a–f** and allenyl phosphine oxides **7a–d** according to the reaction sequence showed in Scheme 3 and Table 3.

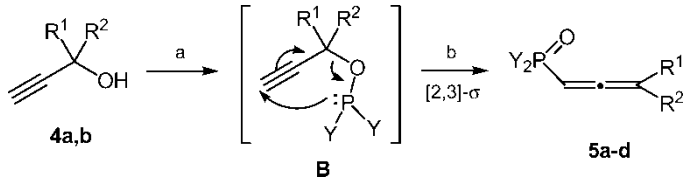
In summary, two convenient and efficient methods for synthesis of a new family of 1,1-diacceptor-substituted allenes have been described. Further studies on these potentially important synthetic methodologies are currently in progress. At the same time, the synthetic application of the prepared 2-sulfonyl-functionalized allenecarboxylates and 1-sulfonyl-functionalized

Table 1. Synthesis of 4-sulfinato-substituted 2-alkynoates **2a–c** and 2-sulfonyl-substituted allenecarboxylates **3a–c** according to Scheme 1

Entry	R	R^1	R^2	Alkyne	Yield[a] (%)	Allene	Yield[a,b] (%)
1	Me	Me	Me	**2a**	73	**3a**	49
2	Me	$-(CH_2)_5-$		**2b**	70	**3a**	45
3	CCl_3	Me	Me	**2c**	72	**3a**	47

[a]Isolated yields by chromatographical purification on silica gel.
[b]Overall yields without isolation of the alkyne.

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014



Scheme 2. Synthesis of phosphorylated allenes. Reagents and conditions: a) Y_2PCl (Y=MeO, Ph), Et_3N, ether, $-12^{\circ}C$; b) 3 mol % HCl, ether, $-12^{\circ}C$ to rt, 3–6 h.

allenephosphonates and allenyl phosphine oxides for preparation of different heterocyclic compounds is now under investigation as a part of our general synthetic strategy for investigation of the score and limitations of the electrophilic cyclization reactions of bifunctionalized allenes. Results of these investigations will be reported in due course.

EXPERIMENTAL

Method of Analysis

^1H and ^{13}C NMR spectra were obtained on a Brucker DRX-250 spectrometer for solutions in $CDCl_3$. Chemical shifts are in parts per million downfield from internal TMS. IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shumen Microanalytical Service Laboratory. The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. Reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purity on TLC plates.

Starting Materials

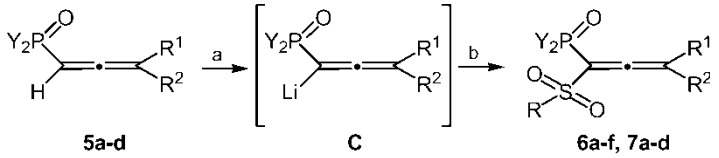
The details of the preparation of the starting dimethyl 3-methyl-buta-1,2-dienylphosphonate (**5a**), dimethyl 2-cyclohexylidene-ethenylphosphonate

Table 2. Synthesis of phosphorylated allenes **5a–d** according to Scheme 2

Entry	Allene	Y	R^1	R^2	Yield[a] (%)
1	**5a**	MeO	Me	Me	86
2	**5b**	MeO	—$(CH_2)_5$—		84
3	**5c**	Ph	Me	Me	75
4	**5d**	Ph	—$(CH_2)_5$—		79

[a]Isolated yields by distillation in vacuo or crystallization.

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014



Scheme 3. Synthesis of 1-sulfonyl-substituted phosphorylated allenes. Reagents and conditions: a) LDA, THF, −78°C, 1 h; b) RSO_2Cl (R = Me, CCl_3, TMSO), THF, −78°C to rt, 1 h.

(**5b**), diphenyl (3-methyl-buta-1,2-dienyl) phosphine oxide (**5c**), and diphenyl (2-cyclohexylidene-ethenyl) phosphine oxide (**5d**) have been described in earlier articles.[20]

Synthesis of Ethoxycarbonyl-Substituted Propargyl Sulfinates 2a–c; General Procedure

To a solution of LDA, generated in situ from diisopropylamine (1.11 g, 11 mmol) and n-BuLi (1.6 M in hexane, 6.25 mL, 10 mmol), in THF (20 mL), was added dropwise a solution of ethyl propynoate **1** (0.98 g, 10 mmol) in THF (10 mL) at −100°C. The reaction mixture was stirred at this temperature for 1 h. After the addition of a solution of acetone (0.58 g, 10 mmol) (for preparation of **2a** and **2c**) or cyclohexanone (0.98 g, 10 mmol) (for preparation of **2b**) in THF (10 mL) at −100°C, the mixture was stirred at the same temperature for 10 min. TMSCl (1.09 g, 10 mmol) in THF (10 mL) was added dropwise at −100°C. After the addition was completed, the mixture was warmed to −10°C and stirred at the same

Table 3. Synthesis of 1-sulfonyl-substituted phosphorylated allenes **6a–f** and **7a–d** according to Scheme 3

Entry	Allene	Y	R	R^1	R^2	Yield[a] (%)
1	**6a**	MeO	Me	Me	Me	53
2	**6b**	MeO	Me	—$(CH_2)_5$—		55
3	**6c**	MeO	CCl_3	Me	Me	51
4	**6d**	Ph	Me	Me	Me	49
5	**6e**	Ph	Me	—$(CH_2)_5$—		51
6	**6f**	Ph	CCl_3	Me	Me	54
7	**7a**	MeO	TMSO	Me	Me	50
8	**7b**	MeO	TMSO	—$(CH_2)_5$—		55
9	**7c**	Ph	TMSO	Me	Me	48
10	**7d**	Ph	TMSO	—$(CH_2)_5$—		52

[a]Isolated yield by chromatographical purification on silica gel.

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

temperature for an additional 10 min. After that, a solution of methanesulfinyl chloride (0.99 g, 10 mmol) (for preparation of **2a** and **2b**) or trichloromethanesulfinyl chloride (2.02 g, 10 mmol) (for preparation of **2c**) in THF (20 mL) was added dropwise to the reaction mixture at -10°C. The mixture was stirred at rt for 1 h, quenched with 2 N HCl, extracted with Et_2O or EtOAc, washed with sat. NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographied on a column (silica gel, Kieselgel Merck 60 F_{254}) using a mixture of EtOAc and hexane (1:4) as an eluent to give the pure propargyl sufinates **2a–c**.

Data

Ethyl 4-methanesulfinyloxy-4-methyl-pent-2-ynoate (2a). Yield: 1.59 g (7.28 mmol; 73%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.28$ (t, 3H, $J = 7.1$ Hz, $MeCH_2O$), 1.64 (s, 6H, 2Me), 3.12 (s, 3H, $MeSO_2$), 4.34 (m, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 13.0$ (CH_3), 30.7 (CH_3), 43.9 (CH_3), 63.2 (C), 64.3 (CH_2), 82.1 (C), 88.4 (C), 152.8 (C). IR (film): 1137 (S=O); 1706 (C=O), 2243 (C≡C); 3286 (HC≡). Anal. calcd. for $C_9H_{14}O_4S$ (218.27): C, 49.52; H, 6.46; S, 14.69. Found: C, 49.60; H, 6.43; S, 14.65.

Ethyl 1-methanesulfinyloxy-cyclohexyl-prop-2-ynoate (2b). Yield: 1.81 g (7.01 mmol; 70%); light yellow solid; mp 83–84°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.18$–2.03 (m, 10H, cyclohexyl), 1.32 (t, 3H, $J = 7.0$ Hz, $MeCH_2O$), 3.14 (s, 3H, $MeSO_2$), 4.28 (m, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 13.2$ (CH_3), 23.1 (CH_2), 26.3 (CH_2), 40.5 (CH_2), 44.4 (CH_3), 62.2 (CH_2), 66.3 (C), 82.5 (C), 91.4 (C), 153.3 (C). IR (nujol): 1142 (S=O); 1712 (C=O), 2250 (C≡C); 3292 (HC≡). Anal. calcd. for $C_{12}H_{18}O_4S$ (258.34): C, 55.79; H, 7.02; S, 12.41. Found: C, 55.68; H, 6.95; S, 12.49.

Ethyl 4-methyl-4-trichloromethanesulfinyloxy-pent-2-ynoate (2c). Yield: 2.34 g (7.28 mmol; 72%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.29$ (t, 3H, $J = 7.0$ Hz, $MeCH_2O$), 1.65 (s, 6H, 2Me), 4.27 (m, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 14.1$ (CH_3), 28.4 (CH_3), 62.5 (C), 64.3 (CH_2), 81.6 (C), 94.41 (C), 129.6 (C), 154.2 (C). IR (film): 1140 (S=O); 1708 (C=O), 2240 (C≡C); 3287 (HC≡). Anal. calcd. for $C_9H_{11}Cl_3O_4S$ (321.61): C, 33.61; H, 3.45; Cl, 33.07; S, 9.97. Found: C, 33.68; H, 3.38; Cl, 33.14; S, 10.04.

Synthesis of 2-Sulfonyl-Substituted Allenecarboxylates 3a–c; General Procedure

A solution of ethoxycarbonyl-substituted prorargyl sulfinate **2** in dried toluene (10 mL) was refluxed for 1 h. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (Kieselgel

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

Merck 60 F_{254}) (eluent: EtOAc–heptane, 1:5) to yield the corresponding 2-sulfonyl-substituted allenecarboxylates **3a–c**.

Data

Ethyl 2-methanesulfonyl-4-methyl-penta-2,3-dienoate (3a). According to the general procedure, propargyl sufinate **2a** (1.59 g, 7.28 mmol) was converted by [2,3]-sigmatropic rearrangement into the allenecarboxylate **3a**. Yield: 0.779 g (3.57 mmol; 49%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.39$ (t, 3H, $J = 7.1$ Hz, $MeCH_2O$), 1.69 (s, 6H, 2Me), 3.00 (s, 3H, $MeSO_2$), 4.30 (m, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 13.9$ (CH_3), 22.1 (CH_3), 41.2 (CH_3), 61.3 (CH_2), 95.3 (C), 103.4 (C), 158.4 (C), 204.3 (C). IR (film): 1127, 1341 (SO_2); 1706 (C═O), 1958 (C═C═C). Anal. calcd. for $C_9H_{14}O_4S$ (218.27): C, 49.52; H, 6.46; S, 14.69. Found: C, 49.58; H, 6.54; S, 14.81.

Ethyl 3-cyclohexylidene-2-methanesulfonyl-acrylate (3b). According to the general procedure, propargyl sufinate **2b** (1.81 g, 7.01 mmol) was converted by [2,3]-sigmatropic rearrangement into the allenecarboxylate **3b**. Yield: 0.815 g (3.15 mmol; 45%); light yellow crystals; mp 71–73°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.37$ (t, 3H, $J = 6.9$ Hz, $MeCH_2O$), 1.50–2.20 (m, 10H, cyclohexylidene), 3.18 (s, 3H, $MeSO_2$), 3.74–4.18 (m, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 14.5$ (CH_3), 24.1 (CH_2), 26.7 (CH_2), 33.5 (CH_2), 39.4 (CH_3), 61.9 (CH_2), 94.8 (C), 104.4 (C), 163.5 (C), 203.7 (C). IR (nujol): 1148, 1350 (SO_2); 1711 (C═O), 1960 (C═C═C). Anal. calcd. for $C_{12}H_{18}O_4S$ (258.34): C, 55.79; H, 7.02; S, 12.41. Found: C, 55.86; H, 7.15; S, 12.47.

Ethyl 4-methyl-2-trichloromethanesulfonyl-penta-2,3-dienoate (3c). According to the general procedure, propargyl sufinate **2c** (2.34 g, 7.28 mmol) was converted by [2,3]-sigmatropic rearrangement into the allenecarboxylate **3c**. Yield: 1.10 g (3.42 mmol; 47%); light yellow crystals; mp 91–92°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.34$ (t, 3H, $J = 6.7$ Hz, $MeCH_2O$), 1.94 (s, 6H, 2Me), 3.68–4.29 (m, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 14.4$ (CH_3), 21.4 (CH_3), 61.8 (CH_2), 95.7 (C), 103.2 (C), 110.8 (C), 157.0 (C), 204.3 (C). IR (nujol): 1146, 1345 (SO_2); 1720 (C═O), 1956 (C═C═C). Anal. calcd. for $C_9H_{11}Cl_3O_4S$ (321.61): C, 33.61; H, 3.45; Cl, 33.07, S, 9.97. Found: C, 33.74; H, 3.39; Cl, 32.94; S, 10.06.

Synthesis of 1-Sulfonyl-Substituted Phosphorylated Allenes 6a–f, 7a–d; General Procedure

To a solution of LDA, generated in situ from diisopropylamine (1.11 g, 11 mmol) and n-BuLi (1.6 M in hexane, 6.25 mL, 10 mmol) in THF (20 ml), was added dropwise a solution of dimethyl 3-methyl-buta-1,2-

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

dienylphosphonate **5a** (1.76 g, 10 mmol) (for preparation of **6a**, **6c**, and **7a**), dimethyl 2-cyclohexylidene-ethenylphosphonate **5b** (2.16 g, 10 mmol) (for preparation of **6b** and **7b**), diphenyl (3-methyl-buta-1,2-dienyl) phosphine oxide **5c** (2.68 g, 10 mmol) (for preparation of **6d**, **6f**, and **7c**), or diphenyl (2-cyclohexylidene-ethenyl) phosphine oxide **6d** (3.08 g, 10 mmol) (for preparation of **6e** and **7d**) in THF (10 mL) at -78°C. The reaction mixture was stirred at this temperature for 1 h. A solution of methanesulfonyl chloride (1.15 g, 10 mmol) (for preparation of **6a**, **6b**, **6d**, and **6e**), trichloromethanesulfonyl chloride (2.18 g, 10 mmol) (for preparation of **6c** and **6f**), or trimethylsilylchlorosulfate (1.89 g, 10 mmol) (for preparation of **7a**–**d**) in THF (10 mL) was added dropwise to the reaction mixture at -78°C. After the addition was completed, the mixture was warmed to rt and stirred for 1 h. Then the mixture was quenched with 2N HCl, extracted with Et_2O, washed with sat. NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographied on column (silica gel, Kieselgel Merck 60 F_{254}) using a mixture of hexane, EtOAc, and Et_2O (3:1:1) as an eluent to give the pure phosphorylated allenes **6a**–**f** and **7a**–**d**.

Data

Dimethyl 1-methanesulfonyl-3-methyl-buta-1,2-dienyl phosphonate (6a). Yield: 2.54 g (5.31 mmol; 53%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.73$ (d, 6H, $J = 7.4$ Hz, 2Me), 3.07 (s, 3H, $MeSO_2$), 3.64 (d, 6H, $J = 12.3$ Hz, 2MeO). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 21.5$ (d, $J_{CP} = 5.1$ Hz, CH_3), 44.0 (d, $J_{CP} = 8.4$ Hz, CH_3), 51.8 (d, $J_{CP} = 14.9$ Hz, CH_3), 94.5 (d, $J_{CP} = 184.8$ Hz, C), 103.1 (d, $J_{CP} = 14.8$ Hz, C), 206.3 (d, $J_{CP} = 4.7$ Hz, C). IR (film): 1054 (P-O-Me); 1122, 1350 (SO_2); 1256 (P═O), 1954 (C═C═C). Anal. calcd. for $C_8H_{15}O_5PS$ (254.24): C, 37.79; H, 5.95; P, 12.18; S, 12.61. Found: C, 37.68; H, 6.00; P, 12.24; S, 12.55.

Dimethyl 2-cyclohexylidene-1-methanesulfonyl-ethenyl phosphonate (6b). Yield: 1.62 g (5.50 mmol; 55%); light yellow solid; mp 101–102°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.40$–2.29 (m, 10H, cyclohexylidene), 3.06 (s, 3H, $MeSO_2$), 3.65 (d, 6H, $J = 12.4$ Hz, 2MeO). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 23.7$ (CH_2), 24.5 (CH_2), 27.1 (d, $J_{CP} = 4.3$ Hz, CH_2), 43.6 (d, $J_{CP} = 8.2$ Hz, CH_3), 52.1 (d, $J_{CP} = 14.8$ Hz, CH_3), 93.9 (d, $J_{CP} = 185.1$ Hz, C), 104.5 (d, $J_{CP} = 14.7$ Hz, C), 205.1 (d, $J_{CP} = 4.3$ Hz, C). IR (nujol): 1048 (P-O-Me); 1130, 1357 (SO_2); 1261 (P═O), 1959 (C═C═C). Anal. calcd. for $C_{11}H_{19}O_5PS$ (294.31): C, 44.89; H, 6.51; P, 10.52; S, 10.90. Found: C, 44.92; H, 6.47; P, 10.47; S, 10.99.

Dimethyl 3-methyl-1-trichloromethanesulfonyl-buta-1,2-dienylphosphonate (6c). Yield: 1.83 g (5.12 mmol; 51%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.75$ (d, 6H, $J = 7.5$ Hz, 2Me), 3.62 (d, 6H, $J = 12.5$ Hz, 2MeO). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 20.4$ (d, $J_{CP} = 5.0$ Hz, CH_3), 53.4 (d, $J_{CP} = 15.1$ Hz, CH_3), 89.7

(d, $J_{CP} = 185.0$ Hz, C), 102.5 (d, $J_{CP} = 14.3$ Hz, C), 107.5 (d, $J_{CP} = 7.8$ Hz, C), 207.7 (d, $J_{CP} = 4.3$ Hz, C). IR (film): 1066 (P-O-Me); 1132, 1363 (SO_2); 1265 (P═O), 1957 (C═C═C). Anal. calcd. for $C_8H_{12}Cl_3O_5PS$ (357.58): C, 26.87; H, 3.38; Cl, 29.74; P, 8.66; S, 8.97. Found: C, 26.76; H, 3.40; Cl, 29.90; P, 8.56; S, 9.05.

Diphenyl (1-methanesulfonyl-3-methyl-buta-1,2-dienyl) phosphine oxide (6d). Yield: 2.04 g (5.89 mmol; 59%); light yellow solid; mp 123–124°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.75$ (d, 6H, $J = 6.5$ Hz, 2Me), 2.97 (s, 3H, $MeSO_2$), 7.88–8.20 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 20.7$ (d, $J_{CP} = 5.3$ Hz, CH_3), 42.4 (d, $J_{CP} = 8.1$ Hz, CH_3), 100.7 (d, $J_{CP} = 183.9$ Hz, C), 106.5 (d, $J_{CP} = 14.3$ Hz, C), 130.2 (d, $J_{CP} = 4.6$ Hz, CH), 132.7 (d, $J_{CP} = 11.4$ Hz, CH), 134.7 (d, $J_{CP} = 7.8$ Hz, CH), 135.6 (d, $J_{CP} = 9.7$ Hz, CH), 138.6 (d, $J_{CP} = 98.5$ Hz, C), 197.4 (d, $J_{CP} = 4.1$ Hz, C). IR (nujol): 1140, 1363 (SO_2); 1203 (P═O), 1952 (C═C═C). Anal. calcd. for $C_{18}H_{19}O_3PS$ (346.38): C, 62.41; H, 5.53; P, 8.94; S, 9.26. Found: C, 62.48; H, 5.49; P, 9.02; S, 9.32.

Diphenyl (2-cyclohexylidene-1-methanesulfonyl-ethenyl) phosphine oxide (6e). Yield: 1.97 g (5.07 mmol; 51%); light yellow solid; mp 132–133°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.41$–2.47 (m, 10H, cyclohexylidene), 2.95 (s, 3H, $MeSO_2$), 7.79–8.22 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 23.9$ (CH_2), 25.2 (CH_2), 26.5 (d, $J_{CP} = 4.5$ Hz, CH_2), 43.0 (d, $J_{CP} = 8.1$ Hz, CH_3), 94.7 (d, $J_{CP} = 187.7$ Hz, C), 105.4 (d, $J_{CP} = 14.8$ Hz, C), 129.5 (d, $J_{CP} = 4.5$ Hz, CH), 133.5 (d, $J_{CP} = 11.1$ Hz, CH), 133.8 (d, $J_{CP} = 8.2$ Hz, CH), 134.1 (d, $J_{CP} = 9.3$ Hz, CH), 139.4 (d, $J_{CP} = 97.2$ Hz, C), 194.5 (d, $J_{CP} = 4.4$ Hz, C). IR (nujol): 1143, 1361 (SO_2); 1198 (P═O), 1957 (C═C═C). Anal. calcd. for $C_{21}H_{23}O_3PS$ (386.45): C, 65.27; H, 6.00; P, 8.02; S, 8.30. Found: C, 65.21; H, 6.14; P, 8.11; S, 8.21.

Diphenyl (3-methyl-1-trichloromethanesulfonyl-buta-1,2-dienyl) phosphine oxide (6f). Yield: 2.43 g (5.40 mmol; 54%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.75$ (d, 6H, $J = 6.5$ Hz, 2Me), 2.97 (s, 3H, $MeSO_2$), 7.88–8.20 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 21.0$ (d, $J_{CP} = 5.2$ Hz, CH_3), 101.5 (d, $J_{CP} = 185.1$ Hz, C), 105.8 (d, $J_{CP} = 14.7$ Hz, C), 109.5 (d, $J_{CP} = 8.4$ Hz, C), 129.3 (d, $J_{CP} = 4.5$ Hz, CH), 134.8 (d, $J_{CP} = 7.9$ Hz, CH), 135.1 (d, $J_{CP} = 11.3$ Hz, CH), 136.2 (d, $J_{CP} = 10.8$ Hz, CH), 142.4 (d, $J_{CP} = 95.5$ Hz, C), 200.5 (d, $J_{CP} = 4.5$ Hz, C). IR (film): 1135, 1349 (SO_2); 1199 (P═O), 1956 (C═C═C). Anal. Calcd. for $C_{18}H_{16}Cl_3O_3PS$ (449.72): C, 48.07; H, 3.59; Cl, 23.65; P, 6.89; S, 7.13. Found: C, 48.15; H, 3.48; Cl, 23.78; P, 8.97; S, 7.31.

Dimethyl 3-methyl-1-trimethylsilyloxysulfonyl-buta-1,2-dienylphosphonate (7a). Yield: 1.64 g (4.99 mmol; 50%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.23$ (s, 9H, Me_3SiO), 1.79 (d, 6H, $J = 7.8$ Hz, 2Me), 3.59 (d, 6H, $J = 11.3$ Hz, 2MeO). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 6.9$ (CH_3), 18.2 (d, $J_{CP} = 5.4$ Hz, CH_3), 51.5 (d, $J_{CP} = 15.0$ Hz, CH_3),

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

95.8 (d, $J_{CP} = 186.7$ Hz, C), 102.9 (d, $J_{CP} = 14.7$ Hz, C), 205.1 (d, $J_{CP} = 4.9$ Hz, C). IR (film): 849 (Si-O-S); 1054 (P-O-Me); 1186, 1319 (SO_2); 1274 (P═O), 1954 (C═C═C). Anal. calcd. for $C_{10}H_{21}O_6PSiS$ (328.40): C, 36.57; H, 6.45; P, 9.43; S, 9.76. Found: C, 36.62; H, 6.39; P, 9.54; S, 9.82.

Dimethyl 2-cyclohexylidene-1-trimethylsilyloxy-sulfonyl-ethenylphosphonate (7b). Yield: 2.02 g (5.48 mmol; 55%); light yellow solid; mp 97–98°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.31$ (s, 9H, Me_3SiO), 1.41–2.49 (m, 10H, cyclohexylidene), 3.61 (d, 6H, $J = 11.5$ Hz, 2MeO). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 7.2$ (CH_3), 23.1 (CH_2), 23.8 (CH_2), 24.9 (d, $J_{CP} = 4.3$ Hz, CH_2), 52.0 (d, $J_{CP} = 15.0$ Hz, CH_3), 94.3 (d, $J_{CP} = 190.5$ Hz, C), 102.8 (d, $J_{CP} = 14.9$ Hz, C), 204.7 (d, $J_{CP} = 5.0$ Hz, C). IR (film): 852 (Si-O-S); 1047 (P-O-Me); 1183, 1324 (SO_2); 1278 (P═O), 1956 (C═C═C). Anal. calcd. for $C_{13}H_{25}O_6PSiS$ (368.46): C, 42.38; H, 6.84; P, 8.41; S, 8.70. Found: C, 42.44; H, 6.77; P, 8.53; S, 8.63.

Diphenyl (3-methyl-1-trimethylsilyloxysulfonyl-buta-1,2-dienyl) phosphine oxide (7c). Yield: 2.02 g (4.80 mmol; 48%); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.23$ (s, 9H, Me_3SiO), 1.85 (d, 6H, $J = 7.7$ Hz, 2Me), 7.55–7.83 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 6.8$ (CH_3), 18.3 (d, $J_{CP} = 5.0$ Hz, CH_3), 94.7 (d, $J_{CP} = 185.9$ Hz, C), 101.3 (d, $J_{CP} = 14.6$ Hz, C), 131.5 (d, $J_{CP} = 11.1$ Hz, CH), 133.2 (d, $J_{CP} = 7.8$ Hz, CH), 133.9 (d, $J_{CP} = 4.9$ Hz, CH), 134.8 (d, $J_{CP} = 9.8$ Hz, CH), 137.4 (d, $J_{CP} = 93.8$ Hz, C), 188.3 (d, $J_{CP} = 4.7$ Hz, C). IR (film): 853 (Si-O-S); 1131, 1347 (SO_2); 1207 (P═O), 1958 (C═C═C). Anal. calcd for $C_{20}H_{25}O_4PSiS$ (420.54): C, 57.12; H, 5.99; P, 7.37; S, 7.63. Found: C, 57.31; H, 6.09; P, 54; S, 7.82.

Diphenyl (2-cyclohexylidene-1-trimethylsilyloxy-sulfonyl-ethenyl) phosphine oxide (7d). Yield: 2.40 g (5.21 mmol; 52%); light yellow solid; mp 102–103°C. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.28$ (s, 9H, Me_3SiO), 1.51–2.48 (m, 10H, cyclohexylidene), 7.68–8.09 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 6.7$ (CH_3), 23.7 (CH_2), 24.9 (CH_2), 26.0 (d, $J_{CP} = 4.8$ Hz, CH_2), 96.5 (d, $J_{CP} = 184.1$ Hz, C), 109.5 (d, $J_{CP} = 14.9$ Hz, C), 129.9 (d, $J_{CP} = 10.3$ Hz, CH), 131.7 (d, $J_{CP} = 7.8$ Hz, CH), 132.0 (d, $J_{CP} = 5.1$ Hz, CH), 134.6 (d, $J_{CP} = 9.9$ Hz, CH), 137.4 (d, $J_{CP} = 95.0$ Hz, C), 191.7 (d, $J_{CP} = 4.9$ Hz, C). IR (nujol): 858 (Si-O-S); 1137, 1351 (SO_2); 1204 (P═O), 1953 (C═C═C). Anal. calcd for $C_{23}H_{29}O_4PSiS$ (460.60): C, 59.97; H, 6.35; P, 6.72; S, 6.96. Found: C, 60.06; H, 6.24; P, 6.81; S, 7.03.

ACKNOWLEDGMENTS

Financial support from the Research Fund of the University of Shumen (Project Nos. 33/2004 and 30/2005) is acknowledged.

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

REFERENCES

1. For Part VI, see Christov, V. C.; Prodanov, B. Bifunctionalized allenes, VI: Synthesis of 3-sulfinylfuran-2(5*H*)-ones and 5*H*-1,2-oxathiole-3-carboxylate 2-oxides by bromination of 2-sulfinyl-2,3-alkadienoates. *Synth. Commun.* **2004**, *34*, 1577–1588.
2. For reviews on the allenes, see (a) Patai, S. Ed.; *The Chemistry of Ketenes, Allenes and Related Compounds*; John Wiley & Sons: New York, 1980; (b) Landor, S. R. Ed.; *The Chemistry of the Allenes*; Academic Press: London, 1982; (c) Pasto, D. J. Recent developments in allene chemistry. *Tetrahedron* **1984**, *40*, 2805; (d) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley & Sons: New York, 1988; (e) Zimmer, R. Alkoxyallenes—building blocks in organic synthesis. *Synthesis* **1993**, 165–178; (f) Elsevier, C. J. In *Methods of Organic Chemistry (Houben-Weyl)*; Helmchen, R. W., Mulzer, J., Schaumann, E., Eds.; Thieme: Stuttgart, 1995; vol. E21a, pp. 537–566; (g) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Wiley-VCH: Weinheim, 2004; vol. 1–2.
3. For reviews on the electrophilic addition to allenes, see (a) Caserio, M. C. Selectivity in addition reactions of allenes. In *Selective Organic Transformations*; Thyagarajan, B. S. Ed.; John Wiley & Sons: New York, 1970; 239–298; (b) Jacobs, T. L. Electrophilic addition to allenes. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 2, pp. 417–509; (c) Smadja, W. Electrophilic addition to allenic derivatives: Chemo-, regio-, and stereochemistry and mechanisms. *Chem. Rev.* **1983**, *83*, 263; (d) Ma, S. M. Ionic additions to allenes. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004; vol. 2, chap. 10, pp. 595–684.
4. For cyclizations of allenic alcohols to 2,5ihydrofurans, see (a) Jacobs, T. L.; Macomber, R.; Zucker, D. Addition reactions of allenes, III: 2,4-Dinitrobenzenesulfenyl chloride and bromine. *J. Am. Chem. Soc.* **1967**, *89*, 7001–7005; (b) Toda, F.; Komora, T.; Akagi, K. A new bromoallene alcohol: Its isolation and reaction. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1493; (c) Hoft, S.; Brandsma, L. Acid-catalyzed ring closure of 1-methoxy-or 1-methylthio-1-(α- or β-hydroxyalkyl)allenes. *Rec. Trav. Chim. Pays-Bas* **1969**, *88*, 845–850; (d) Gelin, R.; Gelin, S.; Albrand, M. Isomerisation en milieu acide d'alcools α-alleniques. *Bull. Soc. Chim. Fr.* **1972**, 720–723; (e) Gelin, R.; Gelin, S.; Albrand, M. Oxymercuration-demercuration d'alcools α-alleniques. *Bull. Soc. Chim. Fr.* **1972**, 1946–1949; (f) Olsson, L.-I.; Claesson, A. Synthesis of 2,5-dihydrofurans and 5,6-dihydro-2*H*-pyrans by silver(I)-catalyzed cyclization of allenic alcohols. *Synthesis* **1979**, 743–745; (g) Beaulieu, P. L.; Morisset, V. M.; Garratt, D. G. The synthesis of 2,5-dihydrofurans from α-allenic alcohols. *Tetrahedron Lett.* **1980**, *21*, 129–132; (h) Marshal, J. A.; Wang, X. [2,3]-Wittig rearrangements of nonracemic (propargyloxy)acetic acids and esters: Synthesis of optically active 2,5-dihydrofurans. *J. Org. Chem.* **1990**, *55*, 2995–2996; (i) Marshal, J. A.; Wang, X. Synthesis of enantioenriched α-hydroxy-α-allenylacetic acids by [2,3]-Wittig rearrangement of α-(propargyloxy)acetates. *J. Org. Chem.* **1991**, *56*, 4913–4918; (j) Marshal, J. A.; Pinney, K. G. Stereoselective synthesis of 2,5-dihydrofurans by sequential S_N2' cleavage of alkynyloxiranes and silver(I)-catalyzed cyclization of the allenylcarbinol products. *J. Org. Chem.* **1993**, *58*, 7180–7184; (k) Ma, S.; Gao, W. Efficient synthesis of 4-(2′-alkenyl)-2,5-dihydrofurans via $PdCl_2$-catalyzed coupling-cyclization reaction of 2,3-allenols with allylic halides. *Tetrahedron Lett.* **2000**, *41*,

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

8933–8936; (l) Krause, N.; Laux, M.; Hoffman-Roder, A. New methods for the stereoselective synthesis of 2-hydroxy-3,4-dienoates and functionalized 2,5-dihydrofurans. *Tetrahedron Lett.* **2000**, *41*, 9613–9616; (m) Hoffman-Roder, A.; Krause, N. Gold(III) chloride catalyzed cyclization of α-hydroxyallenes to 2,5-dihydrofurans. *Org. Lett.* **2001**, *3*, 2537–2538; (n) Krause, N.; Hoffman-Roder, A.; Canisius, J. From amino acids to dihydrofurans: Functionalized allenes in modern organic synthesis. *Synthesis* **2002**, 1759–1774.

5. For electrophilic cyclizations of allencarboxylic acids and esters, see (a) Kohler, E. P.; Whicher, W. J. Optically active α,γ-diphenyl-α-carbomethoxy-γ-naphthylallene. *J. Am. Chem. Soc.* **1940**, *62*, 1489–1490; (b) Aksnes, G.; Froeyen, P. Study of the applicability of the Wittig reaction in synthesis of allenes. *Acta Chim. Scand.* **1968**, *22*, 2347–2347; (c) Shingu, K.; Hagishita, S.; Nakagawa, M. The determination of the absolute configurations of some phenylallenecarboxylic acids. *Tetrahedron Lett.* **1967**, 4371–4374; (d) Kresze, G.; Runge, W.; Ruch, E. Zur stereochemie von allenen, I: Darstellung und optische spaltung einer gruppe von allenic carbonsauren. *Liebigs Ann. Chem.* **1972**, *756*, 112–127; (e) Musierowicz, S.; Wroblewski, A. E.; Krawczyk, H. Stereochemistry of P-chiral phosphinylacetic acid esters I: Asymmetric synthesis of substituted alkadiene-1,2-carboxylic-1 and γ-chiral α,β-unsaturated carboxylic acid esters. *Tetrahedron Lett.* **1975**, 437–440; (f) Kresze, G.; Kloimstein, W. L.; Runge, W. Stereochemie von allenen, III: Cyclisierungreaktionen chiraler 3-phenylallencarbonsauren. *Liebigs Ann. Chem.* **1976**, 979–986; (g) Musierowicz, S.; Wroblewski, A. E. Optically active α,β-unsaturated γ-lactones: Stereospecific transformation of allene carboxylic acids. *Tetrahedron* **1978**, *34*, 461–465; (h) Gill, G. B.; Idris, M. S. H. Synthesis of α,β-unsaturated butenolides from allenic acids. *Tetrahedron Lett.* **1985**, *26*, 4811–4814; (i) Marshal, J. A.; Wallace, E. M.; Soan, P. S. Total synthesis of the pseudopterane ($\pm$)-kallolide B. *J. Org. Chem.* **1995**, *60*, 796–797; (j) Ma, S.; Pan, F.; Hao, X.; Huang, X. Reaction of PhSeCl or PhSCl with 2,3-allenoic acids: An efficient synthesis of β-organoselenium or β-organosulfur substituted butenolides. *Synlett* **2004**, 85–88.
6. For electrophilic cyclizations of sulfur containing allenes, see (a) Horner, L.; Binder, V. Zur chemie der allensulfoxide. *Liebigs Ann. Chem.* **1972**, *757*, 33–68; (b) Braverman, S.; Reisman, D. Electrophilic fragmentation-cyclization of various allenic esters. *Tetrahedron Lett.* **1977**, 1753–1756; (c) Braverman, S.; Reisman, D. An unexpected sulfone to sulfinate transformation: Electrophilic fragmentation-cyclization of diallenic sulfones and propargylic allenesulfinates to α,β-unsaturated γ-sultines. *J. Am. Chem. Soc.* **1977**, *99*, 605–607; (d) Braverman, S.; Duar, Y. Stereochemistry of the electrophilic fragmentation-cyclization of allenic sulfones and sulfinates: Stereoselective synthesis of chiral α,β-unsaturated γ-sultines. *J. Am. Chem. Soc.* **1983**, *105*, 1061–1063.
7. For reviews on the electrophilic cyclizations of phosphonylated allenes, see (a) Angelov, C. M. Five-membered heterocyclization of phosphorus-containing allenes by their reaction with electrophiles—possibilities and restrictions. *Phosphorus Sulfur Relat. Elem.* **1983**, *15*, 177; (b) Khusainova, N. G.; Pudovik, A. N. Phosphorylated allenes: Synthesis and reactions. *Russ. Chem. Rev.* **1987**, *56*, 975; (c) Alabugin, I. V.; Brel, V. K. Phosphorylated allenes: Structure and interaction with electrophiles. *Russ. Chem. Rev.* **1997**, *66*, 205.
8. (a) See Ref. [6a]; (b) Baudin, J.-B.; Julia, S. A.; Wang, Y. Substituted 4-(1′,2′-alkadienesulphinyl)-morpholines; preparation and hydrolytic desulphinylation into the corresponding alkynes. *Tetrahedron Lett.* **1989**, *30*, 4965–4968; (c) Baudin, J.-B.; Bkouche-Waksman, I.; Julia, S. A.; Pascard, C.; Wang, Y. Stereochemical course

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014

of the [2,3]-sigmatropic rearrangement of substituted propargyl N,N-dialkylamidosulfoxylates: X-ray molecular structure of [S*, (S)*R**]-4-[(1,4,4-trimethyl-1,2-pentadienyl)sulfinyl]-morpholine. *Tetrahedron* **1991**, *47*, 3353–3364; (d) Wang, X.; Ni, Z.; Lu, X.; Hollis, A.; Banks, H.; Rodriguez, A.; Padwa, A. [2,3]-Sigmatropic rearrangement of β-phenylsulfonyl propargylic sulfenates as a method for preparing 1,4-bis(phenylsulfonyl)-1,3-butadienes. *J. Org. Chem.* **1993**, *58*, 5377–5385.

9. (a) Braverman, S.; Mechoulam, H. Rearrangement of propargylic benzenesulfinates. *Israel J. Chem.* **1967**, *5*, 71–75; (b) Smith, G.; Stirling, C. J. M. Intramolecular reactions, part IX: Stereochemistry and mechanism of the rearrangement of acetylenic esters of sulphinic and sulphenic acids to allenes. *J. Chem. Soc. C* **1971**, 1530–1535; (c) Braverman, S.; van Asten, P. F. T. M.; van der Linden, J. B.; Zwanenburg, B. A novel synthesis of thiophenes from allenic sulfones involving α,β-unsaturated sulfines as intermediates. *Tetrahedron Lett.* **1991**, *31*, 3867–3870.
10. Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.
11. (a) Braverman, S. Rearrangements involving sulfoxides. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988, chaps. 13, pp. 665–716; (b) Braverman, S. Rearrangements involving sulfoxides. In *In The Chemistry of Sulphones and Sulphones*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988, chap. 14, pp. 717–757.
12. (a) Bestmann, H. J.; Hartung, H. Synthesis of alkyl 2,3-alkadienoates by Wittig reaction. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 214; (b) See Ref. [5b].
13. Miesch, M. Synthesis of α-allenic esters (acids). *Synthesis* **2003**, 746–752, and references cited therein.
14. (a) Coppe-Motte, G.; Borghese, A.; Janousek, Z.; Merenyi, R.; Viehe, H. G. Captodative substitution effect in [2 + 2] cycloadditions between allenes and olefins. *NATO ASI Ser., Ser. C* **1986**, *189*, 371–374; *Chem. Abstr.* **1987**, *107*, 175273w; (b) Conrads, M.; Mattay, J. Convenient methods for the preparation of sulfur substituted allenecarboxylates. *Synthesis* **1991**, 11; (c) Padwa, A.; Bullock, W. H.; Norman, B. H.; Perumattam, J. (Nitroaryl)sulfinyl-substituted allenes: Novel and convenient propargyl alcohol synthons in 4 + 2 cycloaddition chemistry. *J. Org. Chem.* **1991**, *56*, 4252–4259.
15. For a review on the chemistry of alkoxyallenes, see (a) Ref. [2e]; (b) Hoff, S.; Brandsma, L.; Arens, J. R. Preparation, metallation and alkylation of allenyl ethers. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916–924; (c) Hoff, S.; Brandsma, L.; Arens, J. R. Some conversions of allenyl ethers. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1179–1184; (d) Zimmer, R.; Reissig, H.-U. Synthesis of 6*H*-1,2-oxazines by hetero Diels–Alder reactions of nitroso alkenes towards methoxyallenes. *Liebigs Ann. Chem.* **1991**, 553–562; (e) Hormuth, S.; Reissig, H.-U. Diastereoselective additions of lithiated methoxyallene towards chiral aldehydes. *Synlett* **1991**, 179–180.
16. Tsuboi, S.; Kuroda, H.; Takatsuka, S.; Fukawa, T.; Sakai, T.; Utaka, M. A new aldol condensation of α-allenic esters with aldehydes, including a one-pot synthesis of enyne compounds. *J. Org. Chem.* **1993**, *58*, 5952–5957.
17. (a) Brandsma, L.; Wijers, H. E.; Arens, J. R. Chemistry of acetylenic ethers. Allenyl thioethers from alkynyl thioethers. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 1040–1046; (b) see Ref. [6a]; (c) see Ref. [8b]; (d) see Ref. [9c].
18. (a) Horner, L.; Binder, V. Zur chemie der allenphosphinoxide. *Phosphorus* **1971**, *1*, 17–22; (b) Macomber, R. S.; Krudy, G. A.; Amer, M. A. Reactions of

oxaphospholenes, 2: Hydrolysis of neopentyl esters, phenyl esters, and amides. *J. Org. Chem.* **1983**, *48*, 1420–1424; (c) Macomber, R. S.; Hemling, T. C. 139: A Horner–Emmons approach to cumulatrienes. *Israel J. Chem.* **1985**, *26*, 136–139; (d) Macomber, R. S.; Bauer, P. D. Synthetic approaches to molecules with sterically hidden functional groups. *J. Chem. Res., Synop.* **1978**, 194–195; (e) Macomber, R. S.; Hemling, T. C. Synthetic approaches to molecules with sterically hidden functional groups, 2: Bicyclo[8.8.2]eicosa-1(19),10(20),19-triene: The first bicyclic cumulatriene. *J. Am. Chem. Soc.* **1986**, *108*, 343–344.

19. For our previous reports on bifunctionalized allenes, see (a) Christov, V. C.; Prodanov, B. Synthesis of 1-substituted phosphorylated allenes. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *166*, 265–273; (b) Christov, V. C.; Prodanov, B.; Nikolova, R. One-pot synthesis of 2-substituted allenecarboxylates. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *166*, 275–281; (c) Christov, V. C.; Prodanov, B. Bifunctionalized allenes, part III: Bromination of 1-substituted phosphorylated allenes. *Phosphorus, Sulfur Silicon Ralat. Elem.* **2000**, *166*, 243–249; (d) Christov, V. C.; Prodanov, B. Bifunctionalized allenes, part IV: 1,2λ^5-Oxaphosphole-3-carboxylates and 3-phosphoryl-2(5*H*)-furanones from 2-phosphoryl-2,3-alkadienoates. *Heterocycl. Commun.* **2002**, *8*, 349–354; (e) Christov, V. C.; Prodanov, B. Bifunctionalized allenes, part V: 3-Sulfinyl-2,5-dihydro-1,2λ^5-oxaphosphol-2-ones and 3-phosphoryl-1,2λ^4-oxathiol-2(5*H*)-ones from 1-sulfinyl-substituted phosphorylated allenes. *Heterocycles* **2002**, *57*, 1777–1780; (f) see Ref. [1].
20. (a) Boisselle, A. P.; Meinhardt, N. A. Acetylene-allene rearrangements reactions of trivalent phosphorus chlorides with α-acetylenic acohols and glycols. *J. Org. Chem.* **1962**, *27*, 1828–1833; (b) Angelov, C. M.; Mikhailova, T. S.; Ignat'ev, V. M.; Dogadina, A. V.; Ionin, B. I. Synthesis of 1,2-alkadienephosphonic acids derivatives. *Comp. Rend. Acad. Bulg. Sci.* **1979**, *32*, 619; *Chem. Abstr.* **1979**, *92*, 22563 m.

Downloaded by [University of Washington Libraries] at 21:00 06 November 2014