HETEROCYCLES, Vol. 98, No. 9, 2019, pp. 1236 - 1243. © 2019 The Japan Institute of Heterocyclic Chemistry
Received, 17th July, 2019, Accepted, 28th August, 2019, Published online, 20th September, 2019
DOI: 10.3987/COM-19-14136

TRIFUNCTIONALIZED ALLENES. PART VI. SYNTHESIS OF 2,5-DIHYDRO-1,2-OXAPHOSPHOLES, FURAN-2(5*H*)-ONES AND 5,6-DIHYDRO-2*H*-PYRANS BY ELECTROPHILIC CYCLIZATION AND CYCLOISOMERIZATION OF 4-PHOSPHORYLATED 6-HYDROXYHEPTA-2,3-DIENOATES†

Ismail E. Ismailov, Ivaylo K. Ivanov, and Valerij Ch. Christov*

Department of Chemistry, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115, Universitetska str., BG-9712 Shumen, Bulgaria; E-Mail: vchristo@shu.bg

†This article is dedicated to Prof. Dr. Toru Minami from Kyushu Institute of Technology, Tobata, Kitakyushu, Japan on the occasion of his 80th birthday.

Abstract – We have synthesized model compounds of three types heterocyclic compounds by electrophilic cyclization and cycloisomerization of 4-phosphorylated 6-hydroxyhepta-2,3-dienoates. Reactions with electrophiles produce mixtures of the 2,5-dihydro-1,2-oxaphosphole-5-carboxylates and the 5-phosphorylfuran-2(5*H*)-ones by competitive electrophilic cyclization due to the neighboring phosphonate (phosphine oxide) and the carboxylate groups participation. Starting compounds were smoothly converted into the corresponding 4-phosphoryl-5,6-dihydro-2*H*-pyran-2-carboxylates, by using 5 mol% of a silver salt as a catalyst in the 6-*endo*-*trig* cycloisomerization reaction.

Allenes are versatile building blocks with broad applications in modern synthetic chemistry,[1] and are extremely important subunits in a variety of natural products and pharmaceutical molecules.[1b,1e,2] Phosphorylated allenes including allenylphosphonates and phosphine oxides are an important class of allene-containing, extremely versatile reagents in organic chemistry, especially for the preparation of structurally diverse organophosphorus compounds and phosphorus heterocyclic compounds.[3] Literature data on the reactions of phosphorylated allenes (phosphonates, phosphinates, and phosphine oxides) with electrophilic reagents show that depending on the structure of the starting allenic compound as well as the type of the electrophile, the reactions proceed with cyclization of the allenic system bearing phosphoryl

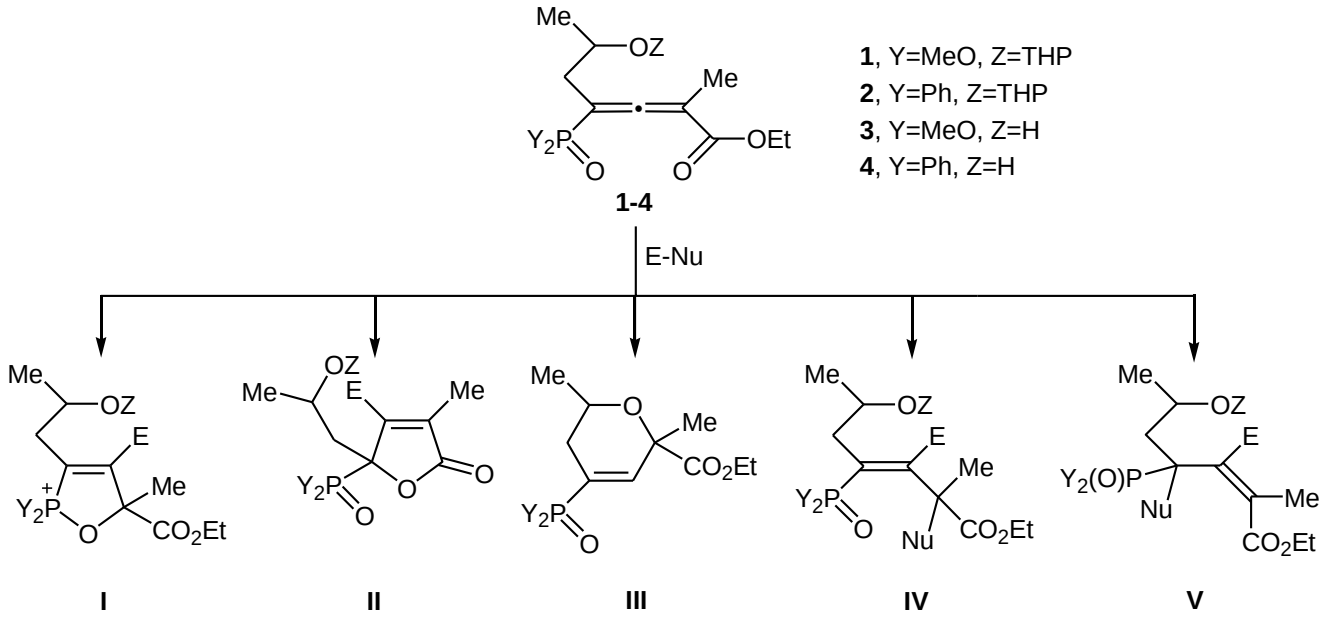
group (O=P-C=C=C) to give heterocyclic compounds in most cases.[4,5]

Furan-2(5*H*)-ones (*γ*-lactones) are important intermediates in organic synthesis[6] and much attention has been paid to the development of efficient and diverse synthetic methods for construction of this five-membered ring system.[6] Among these, cyclization involving allenecarboxylic acids and their derivatives, the so-called lactonization reaction, is one of the most efficient pathways.[7]

On the other hand, transition metal-catalyzed cyclization of functionalized allenes bearing a nucleophilic center has attracted considerable attention in recent years.[8] Particularly, the cyclization reactions of allenols catalyzed by Ag(I),[9] Hg(II),[10] Pd(0),[11] Pd(II),[12] Ru(III),[13] Au(I),[14] and Au(III)[15] have become quite useful methodologies for the synthesis of five- or six-membered oxygen-containing heterocycles. Intramolecular cyclization of the diethylphosphono-substituted α-allenic alcohols in the presence of $AgNO_3$[16a] and $CuCl_2$[16b] yielded 3,6-dihydro-2*H*-pyran-4-yl- and 4,5-dihydro-3-furanylphosphonates.

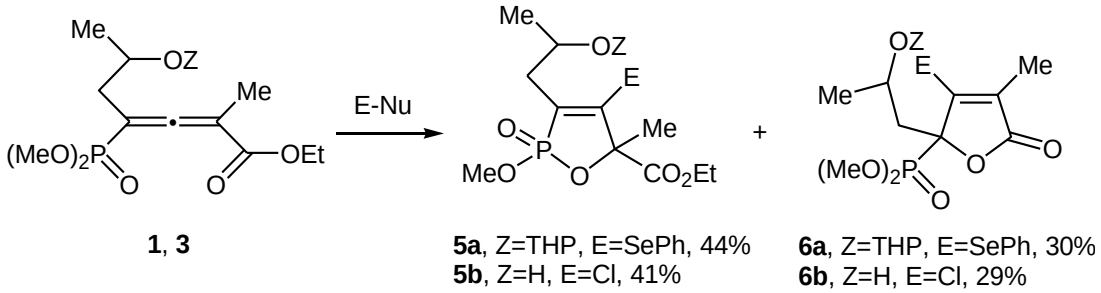
Our long-standing research program focuses on the synthesis and the development of efficient cyclization reactions of trifunctionalized allenes. More specifically, our attention is drawn to 4-phosphorylated 6-hydroxyhepta-2,3-dienoates as 1,1,3-trifunctionalized allenes. These molecules can be considered a combination of an allenephosphonate or allenylphosphine oxide, an allenecarboxylate and a hydroxyallene and they are supposed to have different reactivity profiles in cyclization reactions. In a continuation to our communications[18] on the synthesis and cyclization reactions of the bifunctionalized allenes, in this paper, we present recent results of our studies dedicated towards the electrophilic cyclization and cycloisomerization reactions of 4-phosphorylated 6-hydroxyhepta-2,3-dienoates, which strongly improve the scope of this method for synthesis of heterocyclic compounds.

We applied a convenient, efficient, atom economical and regioselective four-step method[17] to achieve a range of the 4-phosphorylated 6-hydroxyhepta-2,3-dienoates **1-4**. The present paper is a recent part of our long-term objective to investigate both the scope and the limitations of the electrophilic cyclization and cycloisomerization reactions of the trifunctionalized allenes, namely the phosphorylated hydroxyallenecarboxylates. It is necessary to draw attention to the fact that conceptually three distinct modes of cyclization of the 4-phosphorylated 6-hydroxyhepta-2,3-dienoates **1-4** are possible. They depend on the electrophilic atom that forms a new bond with the central carbon of the allenic system, which seems likely.[4,5,19] It is evident that these pathways are closely connected with the intramolecular neighboring group participation of the phosphoryl, ethoxycarbonyl and/or the hydroxymethyl groups as internal nucleophile(s) in the final step of the cyclization. Besides the 5-*endo-trig* cyclizations[20] to the 2,5-dihydro-1,2-oxaphosphole-5-caboxylates **I**, the 5-phosphoryl-furan-2(5*H*)-ones **II** or the 4-phosphoryl-5,6-dihydro-2*H*-pyran-2-carboxylates **III**, the electrophilic addition might afford the 2,3-adducts **IV** and/or the 2,1-adducts **V** (**Scheme 1**).



Scheme 1

We started the present study with the reaction of the 4-(dimethoxyphosphoryl)-6-hydroxyhepta-2,3-dienoates with protected (**1**) or unprotected (**3**) hydroxy group with benzeneselenenyl chloride or sulfuryl chloride (**Scheme 2**). We conducted the reactions under the optimized reaction conditions determined in the similar reactions of the bifunctionalized allenes[18a,b,d] – solvent CH_2Cl_2 at -20 °C using 1.0 *equiv* of the allenephosphonate and 1.2 *equiv* of the electrophilic reagent. We have to say that the reaction under this set of standard reaction conditions in the favored 5-*endo-trig* mode affords mixtures of the 2-oxo-2,5-dihydro-1,2-oxaphosphole-5-carboxylates **5** and 5-(dimethylphosphoryl)furan-2(5*H*)-ones **6** in the ratio 1.47:1 and 1.41:1 by competitive electrophilic cyclization of the 4-phosphorylated 6-hydroxyhepta-2,3-dienoates **1** and **3** with the neighboring group participation of phosphonate and carboxylate groups in the cyclization in very good overall yields (74 and 70%).



1, **3**

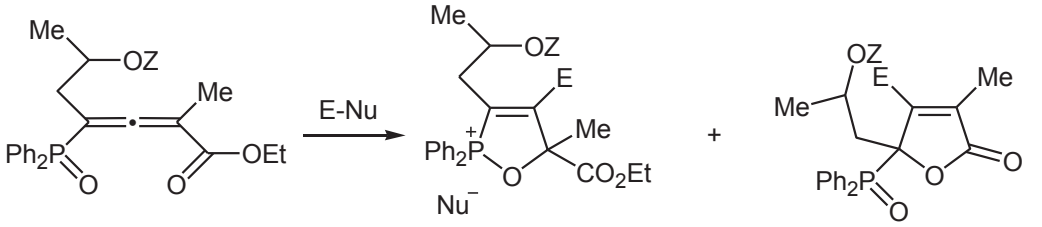
5a, Z=THP, E=SePh, 44%
5b, Z=H, E=Cl, 41%

6a, Z=THP, E=SePh, 30%
6b, Z=H, E=Cl, 29%

Scheme 2

To outline the general terms of this methodology, the reaction of the 4-(diphenylphophinoyl)-6-hydroxyhepta-2,3-dienoates with protected and unprotected hydroxy group **2** and **4** with bromine or benzensulfenyl chloride was investigated. Surprisingly, once we applied the current standard conditions

to the 1,1,3-trifunctionalized allenes comprising a phosphine oxide, an ethoxycarbonyl and a hydroxymethyl groups such as **2** and **4** (**Scheme 3**), the interaction afforded mixtures of the 5-ethoxycarbonyl-2,5-dihydro-1,2-oxaphosphol-2-ium chlorides **7** and 5-(diphenylphosphinoyl)-furan-2(5*H*)-ones **8** in overall yields (75% and 73%) in the ratio 1.78:1 and 1.81:1. These reaction pathways may be interpreted as a result of the neighboring phosphine oxide and ethoxycarbonyl groups participation as the internal nucleophiles in the favored 5-*endo-trig* mode cyclization.



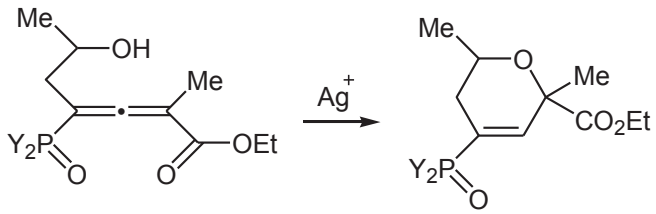
2, **4**

7a, Z=THP, E=Br, 48%
7b, Z=H, E=SPh, 47%

8a, Z=THP, E=Br, 27%
8b, Z=H, E=SPh, 26%

Scheme 3

In addition to the above mentioned preparation of the 2,5-dihydro-1,2-oxaphosphole-5-caboxylates **5** and **7** and the 5-phosphorylfuran-2(5*H*)-ones **6** and **8** by electrophilic cyclization of the 4-phosphorylated 6-hydroxyhepta-2,3-dienoates **1-4** due to the phosphonate (phosphine oxide) or carboxylate neighboring group participation in the 5-*endo-trig* mode cyclization, the next step in our study was to explore the possibilities of the cycloisomerization reaction of the above phosphorylated hydroxyallenecarboxylates **3** and **4** in the presence of silver salts as catalysts. We conducted the reaction under the optimized reaction conditions determined in the similar reactions of the phosphorylated (α-hydroxy)-[18c,e] and (β-hydroxy)-[18f,e] allenes earlier – solvent methylene chloride, 5 mol% catalyst and room temperature. The reaction occurred *via* a 6-*endo-trig* cyclization and the hydroxy group participates as an internal nucleophile to give the 4-phosphoryl-5,6-dihydro-2*H*-pyran-2-carboxylates **9** (**Scheme 4**).



3, **4**

9a, Y=MeO, 74% (Method A); 51% (Method B)
9b, Z=Ph, 70% (Method A); 47% (Method B)

Scheme 4

In conclusion, we have developed the competitive electrophilic cyclization and silver-catalyzed cycloisomerization reactions of the 4-phosphorylated 6-hydroxyhepta-2,3-dienoates, which provided an efficient route to 2,5-dihydro-1,2-oxaphospholes, 5-phosphorylated furan-2(5*H*)-ones and

4-phosphorylated 5,6-dihydro-2*H*-pyrans which are produced as a result of the participation of the neighboring phosphonate (phosphine oxide), carboxylate or hydroxy groups as internal nucleophiles in the 5- or 6-*endo-trig* cyclization processes. The successful synthesis of these compounds opens a new access to novel heterocyclic molecules with interesting properties as well as broad range biological activities.

EXPERIMENTAL

General Procedure for the Electrophilic Cyclization Reactions of the 4-Phosphorylated 6-Hydroxy-2-methylhepta-2,3-dienoates 1–4.

To a solution of the 4-phosphorylated 6-hydroxy-2-methylhepta-2,3-dienoates with protected (**1** or **2**) or unprotected (**3** or **4**) hydroxy group (3.0 mmol) in dry CH_2Cl_2 (10 mL) at -20 °C was added dropwise with stirring a solution of electrophilic reagent (sulfuryl chloride, bromine, benzenesulfenyl chloride or benzeneselenenyl chloride) (3.6 mmol) in the same solvent (10 mL). The reaction mixture was stirred at the same temperature for 3 h (**5** and **6**) and 5 h (**7** and **8**) at room temperature. After evaporation of the solvent, the residue was purified by column chromatography on a silica gel with EtOAc/hexane. The pure products **5** and **6** had the following properties:

Ethyl 2-Methoxy-5-methyl-2-oxo-4-phenylselenenyl-3-(2-tetrahydro-2*H*-pyran-2-yloxypropyl)-2,5-dihydro-1,2-oxaphosphole-5-carboxylate 5a. Orange oil, yield: 44%. Eluent for TLC: EtOAc:hexane = 1:5, R_f 0.44; IR (neat, cm^{-1}): 1022 (C-O-P), 1125 (C-O-C), 1269 (P=O), 1438, 1491 (Ph), 1581 (C=C), 1726 (C=O). ^{1}H NMR (600.1 MHz): δ 1.10-1.27 (m, 6H, OTHP), 1.29 (t, *J*=6.8 Hz, 3H, MeCH$_2$O), 1.33 (d, *J*=6.3 Hz, 3H, MeCH), 1.76 (s, 3H, MeC=), 2.63-2.74 (m, 2H, CH_2), 3.50-3.65 (m, 2H, OTHP), 3.74 (d, *J*=11.4 Hz, 3H, MeO), 4.10-4.24 (m, 1H, MeCH), 4.16 (q, *J*=6.8 Hz, 2H, MeCH$_2$O), 4.56-4.63 (m, 1H, OTHP), 7.38-7.46 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ 14.0 (CH_3), 20.1 (CH_2), 21.9 (*J*=7.8, CH_3), 22.9 (*J*=4.5, CH_3), 26.1 (CH_2), 32.2 (CH_2), 37.3 (*J*=5.8, CH_2), 52.0 (*J*=14.8, CH_3), 62.4 (CH_2), 64.1 (CH_2), 70.2 (*J*=8.2, CH), 91.5 (*J*=10.0 Hz, C), 96.2 (CH), 128.0 (*J*=101.5 Hz, C), 128.3-140.1 (Ph), 168.5 (*J*=15.3 Hz, C), 183.5 (*J*=8.2 Hz, C). ^{31}P NMR (242.9 MHz): δ_P 33.4. HRMS (ESI): *m/z* calcd for $C_{22}H_{32}O_7PSe$ $[M+H]^+$ 518.4190, found 518.4221. Anal. Calcd for $C_{22}H_{31}O_7PSe$: C 51.07, H 6.04. Found: C 51.03, H 6.09.

Dimethyl [4-Methyl-5-oxo-3-phenylselenenyl-2-(2-tetrahydro-2*H*-pyran-2-yloxypropyl)-2,5-dihydrofuran-2-yl]phosphonate 6a. Light yellow oil, yield: 30%. Eluent for TLC: EtOAc:hexane = 1:5, R_f 0.65; IR (neat, cm^{-1}): 1125 (C-O-C), 1269 (P=O), 1439, 1490 (Ph), 1622 (C=C), 1747 (C=O). ^{1}H NMR (600.1 MHz): δ 1.11-1.25 (m, 6H, OTHP), 1.38 (d, *J*=5.9 Hz, 6H, MeCH), 2.11 (s, 3H, MeC=), 2.50-2.71 (m, 2H, CH_2), 3.64-3.77 (m, 2H, OTHP), 3.85 (d, *J*=10.5 Hz, 6H, MeO), 4.38-4.48 (m, 1H, MeCH), 4.54-4.59 (m, 1H, OTHP), 7.31-7.94 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ 16.7 (*J*=5.3, CH_3),

20.1 (CH_2), 24.1 (J=5.2, CH_3), 26.0 (CH_2), 31.6 (CH_2), 38.1 (J=5.7, CH_2), 53.7 (J=5.9, $2CH_3$), 63.4 (CH_2), 67.2 (J=7.8 Hz, CH), 96.0 (CH), 102.3 (J=126.5 Hz, C), 128.1 (J=7.9 Hz, C), 128.4-138.7 (Ph), 175.0 (J=8.0 Hz, C), 176.8 (J=15.0 Hz, C). ^{31}P NMR (242.9 MHz): δ_P 15.3. HRMS (ESI): *m/z* calcd for $C_{21}H_{30}O_7PSe$ $[M+H]^+$ 504.3925, found 504.3902. Anal. Calcd for $C_{21}H_{29}O_7PSe$: C 50.11, H 5.81. Found: C 50.17, H 5.85.

Procedure for Silver-Catalyzed Cycloisomerization of the 4-Phosphorylated 6-Hydroxy-2-methylhepta-2,3-dienoates 3 and 4

Method A: Silver perchlorate (0.15 mmol) was added to a solution of the 4-phosphorylated 6-hydroxy-2-methylhepta-2,3-dienoates **3** or **4** (3.0 mmol) in dry CH_2Cl_2 (10 mL). The mixture was stirred at room temperature in the dark for 7 h (for **3**) and 9 h (for **4**). Saturated sodium chloride solution was added to precipitate the silver ions. The product was extracted by $CHCl_3$. The organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on a column with a mixture of EtOAc and hexane as an eluent to give the pure products **9** as oils.

Method B: The 4-phosphorylated 6-hydroxy-2-methylhepta-2,3-dienoates **3** or **4** (3.0 mmol) is dissolved in 40:60 water/acetone (10 mL) containing calcium carbonate (1 mmol) and silver nitrate (0.3 mmol). The mixture was stirred at room temperature in the dark for 12 h (for **3**) and 15 h (for **4**). The product is taken up in Et_2O and the ether solution is washed with saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a column with a mixture of EtOAc and hexane as an eluent to give the pure products **9** as oils, which had the following properties:

Ethyl 4-(Diphenylphosphinoyl)-2,6-dimethyl-5,6-dihydro-2*H*-pyran-2-carboxylate 9b. Yellow oil, yield: 70% (Method A), 47% (Method B). Eluent for TLC: EtOAc:hexane:hexane = 1:2, R_f 0.48; IR (neat, cm^{-1}): 1124 (C-O-C), 1177 (P=O), 1440, 1494 (Ph), 1619 (C=C), 1724 (C=O). ^{1}H NMR (600.1 MHz): δ 1.25 (t, J=6.7 Hz, 3H, MeCH$_2$O), 1.30-1.36 (m, 3H, MeCHO), 1.59 (s, 3H, MeC), 2.33-2.58 (m, 2H, CH_2), 3.59-3.72 (m, 1H, MeCHO), 4.15 (q, J=6.7 Hz, 2H, MeCH$_2$O), 6.94-7.05 (m, 1H, =CH). 7.44-7.77 (m, 10H, 2Ph). ^{13}C NMR (150.9 MHz): δ 13.8 (CH_3), 21.8 (J=4.7 Hz, CH_3), 27.1 (J=5.2 Hz, CH_3), 39.2 (J=6.0 Hz, CH_2), 63.5 (CH_2), 70.5 (J=7.9 Hz, CH), 71.4 (J=7.8 Hz, C), 128.4-135.3 (2Ph), 132.7 (J=175.4 Hz, C), 144.5 (J=7.9 Hz, CH), 175.9 (J=4.6 Hz, C). ^{31}P NMR (242.9 MHz): δ_P 37.0. HRMS (ESI): *m/z* calcd for $C_{22}H_{26}O_4P$ $[M+H]^+$ 385.4132, found 385.4167. Anal. Calcd for $C_{22}H_{25}O_4P$: C 68.74, H 6.56. Found: C 68.89, H 6.71.

ACKNOWLEDGEMENTS

Financial support by the Research Fund of the Konstantin Preslavsky University of Shumen under Projects Nos. RD-08-158/2018 and RD-08-94/2019 is gratefully acknowledged.

REFERENCES

1. (a) H. F. Schuster and G. M. Coppola, 'Allenes in Organic Synthesis', Wiley, New York, 1984; (b) *Modern Allene Chemistry*, ed. by N. Krause and A. S. K., Hashmi, Wiley-VCH, Weinheim, 2004; (c) M. Brasholz, H.-U. Reissig, and R. Zimmer, *Acc. Chem. Res.*, 2009, **42**, 45; (d) S. Ma, *Acc. Chem. Res.,* 2009, **42**, 1679; (e) S. Yu and S. Ma, *Angew. Chem. Int. Ed.*, 2012, **51**, 3074.
2. A. Hoffmann-Röder and N. Krause, *Angew. Chem. Int. Ed.*, 2004, **43**, 1196.
3. (a) F. Yu, X. Lian, and S. Ma, *Org. Lett.*, 2007, **9**, 1703; (b) F. Yu, X. Lian, J. Zhao, Y. Yu, and S. Ma, *J. Org. Chem.*, 2009, **74**, 1130; (c) P. Li, Z.-J. Liu, and J.-T. Liu, *Tetrahedron*, 2010, **66**, 9729; **(**d) N. Xin and S. Ma, *Eur. J. Org. Chem.*, 2012, 3806; (e) P. Fourgeaud, J.-N. Volle, J.-P. Vors, Y.-A. Bekro, J.-L. Pirat, and D. Virieux, *Tetrahedron*, 2016, **72**, 7912; (f) I. Essid, C. Laborde, F. Legros, N. Sevrain, S. Touil, M. Rolland, T. Ayad, J.-N. Volle, J.-L. Pirat, and D. Virieux, *Org. Lett.*, 2017, **19**, 1882.
4. (a) C. M. Angelov and C. Z. Christov, *Synthesis*, 1984, 664; (b) F. Yu, X. Lian, J. Zhao, Y. Yu, and S. Ma, *J. Org. Chem.*, 2009, **74**, 1130; For reviews, see: (c) C. M. Angelov, *Phosphorus, Sulfur Silicon Relat. Elem.,* 1983, **15**, 177; (d) N. G. Khusainova and A. N. Pudovik, *Russ. Chem. Rev.,* 1987, **56**, 564; (e) I. V. Alabugin and V. K. Brel, *Russ. Chem. Rev.*, 1997, **66**, 205; (f) S. Ma, *Acc. Chem. Res.*, 2009, **42**, 1679; (g) V. K. Brel, *Heteroat. Chem.*, 2006, **17**, 547.
5. (a) C. M. Angelov, C. Z. Christov, and B. I. Ionin, *Zh. Obshch. Khim.*, 1982, **52**, 264; (b) N. G. Khusainova, L. V. Naumova, E. A. Berdnikov, and A. N. Pudovik, *Zh. Obshch. Khim.*, 1982, **52**, 1040; (c) D. D. Enchev, C. M. Angelov, E. Krawchik, A. Skowronska, and J. Michalski, *Phosphorus, Sulfur Silicon Relat. Elem.,* 1991, **57**, 249.
6. For reviews, see (a) Y. S. Rao, *Chem. Rev.*, 1964, **64**, 353; (b) Y. S. Rao, *Chem. Rev.*, 1976, **76**, 625; (c) D. W. Knight, *Contemp. Org. Synth.*, 1994, 287.
7. (a) E. P. Kohler and W. J. Whitcher, *J. Am. Chem. Soc.*, 1940, **62**, 1489; (b) K. Shingu, S. Hagishita, and M. Nakagawa, *Tetrahedron Lett.*, 1967, 4371; (c) S. Ma and S. Wu, *Tetrahedron*, 1999, **55**, 12137; (d) S. Ma and S. Wu, *Tetrahedron Lett.*, 2001, **42**, 4075; (e) S. Ma, F. Pan, X. Hao, and X. Huang, *Synlett*, 2004, 85; (f) C. Fu and S. Ma, *Eur. J. Org. Chem.*, 2005, 3942; (g) G. Chen, C. Fu, and S. Ma, *Tetrahedron*, 2006, **62**, 4444; (h) C. Zhou, Z. Ma, Z. Gu, C. Fu, and S. Ma, *J. Org. Chem.*, 2008, **73**, 772.
8. For review, see: R. Zimmer, C. U. Dinesh, E. Nadanan, and F. A. Khan, *Chem. Rev.*, 2000, **100**, 3067.
9. (a) L.-I. Olsson and A. Claesson, *Synthesis*, 1979, 743; (b) S. S. Nikam, K. H. Chu, and K. K. Wang, *J. Org. Chem.*, 1986, **51**, 745; (c) J. A. Marshall, R. H. Yu, and J. F. Perkins, *J. Org. Chem.*, 1995, **60**, 5550.

10. J. -J. Chilot, A. Doutheau, and J. Gore, *Tetrahedron Lett.*, 1982, **23**, 4693.
11. (a) K. Uemura, D. Shiraishi, M. Noziri, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1063; (b) S.-K. Kang, T. Yamaguchi, S.- J. Pyun, Y.-T. Lee, and T.-G. Baik, *Tetrahedron Lett.*, 1998, **39**, 2127.
12. (a) S. Ma and W. Gao, *Tetrahedron Lett.*, 2000, **41**, 8933; (b) S. Ma and W. Gao, *J. Org. Chem.*, 2002, **67**, 6104.
13. (a) E. Yoneda, T. Kaneko, S.-W. Zhang, K. Onitsuka, and S. Takahashi, *Org. Lett.*, 2000, **2**, 441; (b) B. M. Trost and A. B. Pinkerton, *J. Am. Chem. Soc.*, 1999, **121**, 10842.
14. (a) A. Hoffmann-Röder and N. T. Krause, *Org. Biomol. Chem.*, 2005, **3**, 387; (b) R. A. Widenhoefer and X. Han, *Eur. J. Org. Chem.*, 2006, 4555; (c) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem. Int. Ed.*, 2006, **45**, 7896; (d) E. Jimenez-Nunez and A. M. Echavarren, *Chem. Commun.*, 2007, 333; (e) D. J. Gorin and F. D. Toste, *Nature*, 2007, **446**, 395; (f) N. Bongers and N. Krause, *Angew. Chem. Int. Ed.*, 2008, **47**, 2178.
15. (a) A. Hoffman-Röder and N. Krause, *Org. Lett.*, 2001, **3**, 2537; (b) N. Krause, A. Hoffman-Röder, and J. Canisius, *Synthesis*, 2002, 1759; (c) C. Deutsch, B. Gockel, A. Hoffmann-Röder, and N. Krause, *Synlett*, 2007, 1790.
16. (a) V. K. Brel, *Synthesis*, 1999, 463; (b) V. K. Brel and E. V. Abramkin, *Mendeleev Commun.*, 2002, **12**, 64.
17. I. E. Ismailov, I. K. Ivanov, and V. C. Christov, *Bulg. Chem. Commun., Special Ed. B*, 2017, **49**, 33.
18. (a) V. C. Christov, I. K. Ivanov, and I. E. Ismailov, *Heterocycles*, 2013, **87**, 1903; (b) I. K. Ivanov, I. D. Parushev, and V. C. Christov, *Heteroat. Chem.*, 2014, **25**, 60; (c) I. E. Ismailov, I. K. Ivanov, and V. C. Christov, *Molecules*, 2014, **19**, 11056; (d) V. C. Christov, I. E. Ismailov, and I. K. Ivanov, *Molecules*, 2015, **20**, 7263; (e) H. H. Hasanov, I. K. Ivanov, and V. C. Christov, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2018, **193**, 611; (f) H. H. Hasanov, I. K. Ivanov, and V. C. Christov, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2018, **193**, 797; (g) H. H. Hasanov, I. K. Ivanov, and V. C. Christov, *Heteroat. Chem.*, 2017, **28**, e21357.
19. (a) M. C. Caserio, 'Selectivity in Addition Reactions of Allenes' in 'Selective Organic Transformations', ed. by B. S. Thyagarajan, John Wiley & Sons, New York, 1970, pp. 239-299; (b) P. B. D. De la Mare and R. Bolton, 'Electrophilic Addition to Unsaturated Systems', Elsevier, Amsterdam, 1982, pp. 317-325; (c) T. L. Jacobs, 'Electrophilic Addition to Allenes', in 'The Chemistry of the Allenes', ed. by S. R. Landor, Academic Press, New York, 1982; Vol. 2, pp. 417-510; (d) W. Smadja, *Chem. Rev.*, 1983, **83**, 263; (e) S. Ma, 'Ionic Addition to Allenes' in 'Modern Allene Chemistry', ed. by N. Krause and A. S. K. Hashmi, Wiley-VCH, 2004; Vol. 2, pp. 595-699.
20. J. E. Baldwin, *Chem. Commun.*, 1976, 734.