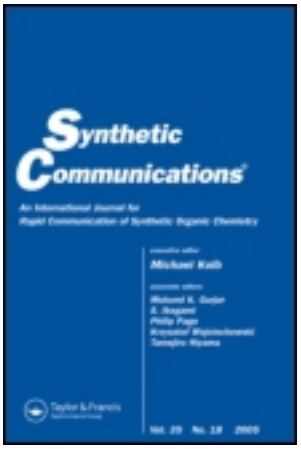


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis and Electrophilic Cyclization Reactions of Diphenyl 3-Methylpenta-1,2,4-trienyl Phosphine Oxide

Ivaylo K. Ivanov [a] & Valerij C. Christov [a]

[a] Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, Shumen, Bulgaria

Accepted author version posted online: 09 May 2012.Version of record first published: 21 Dec 2012.

To cite this article: Ivaylo K. Ivanov & Valerij C. Christov (2013): Synthesis and Electrophilic Cyclization Reactions of Diphenyl 3-Methylpenta-1,2,4-trienyl Phosphine Oxide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 43:6, 800-809

To link to this article: http://dx.doi.org/10.1080/00397911.2011.609957

Synthetic Communications®, 43: 800–809, 2013

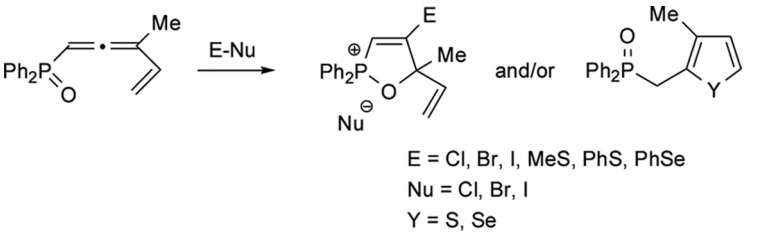
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.609957

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND ELECTROPHILIC CYCLIZATION REACTIONS OF DIPHENYL 3-METHYLPENTA-1,2,4-TRIENYL PHOSPHINE OXIDE

Ivaylo K. Ivanov and Valerij C. Christov
Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, Shumen, Bulgaria

GRAPHICAL ABSTRACT



Abstract *Diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide can be readily prepared via an atom-economical [2,3]-sigmatropic rearrangement of the mediated alkenynyl phosphinite formed in situ by reaction of 3-methylpent-1-en-4-yn-3-ol with diphenylchlorophosphine. Electrophilic cyclization reactions of the vinylallenyl phosphine oxide prepared were investigated as it was established that the reactions proceeded with formation of various heterocyclic or highly unsaturated compounds with participation of the allenic and/or 1,3-dienic part of the vinylallenic system with neighboring group participation of phosphoryl and/or vinylic group.*

Supplemental materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *to view the free supplemental file.*

Keywords 2,5-Dihydro-1,2-oxaphosphole; electrophilic cyclization; neighboring group participation; selenophene; thiophene; 3-vinylallenyl phosphine oxide

INTRODUCTION

In the past three decades, synthesis and use of allene derivatives have been expanded in preparative organic chemistry. The presence of two π electron clouds separated by a single sp hybridized carbon atom is the identifying structural

Received July 20, 2011.

Dedicated to Professor Dr. Toru Minami from Kyushu Institute of Technology, Kitakyushu, Japan, on the occasion of his 70th birthday.

Address correspondence to Valerij C. Christov, Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115 Universitetska str., BG-9700, Shumen, Bulgaria. E-mail: vchristo@shu-bg.net

characteristic of allenes, and it is this unique structural and electronic arrangement that is responsible for the extraordinary reactivity profile displayed by allenic compounds.[1] The synthetic potential of functionalized allenes has been explored extensively in recent years, and this has led to the development of novel methods for the construction of a variety of functionalized heterocyclic and carbocyclic systems.[2] An impressive number of heterocyclic systems have been prepared from allenic starting materials.

One of the characteristic reactions of the allenes is the electrophilic addition reactions in which the addition products of the reagent to the one and/or other double bond of the allenic system are usually obtained.[3] Functionalized allenes are very interesting substrates as a material of choice to study the electrophilic addition reactions on the carbon–carbon double bonds.[4–6] Unlike the allenic hydrocarbons, the presence of a functional group linked to the allenic system considerably changes the course of the reactions with electrophilic reagents. It has been shown[4–6] that the reactions proceeded with cyclization of the allenic system bearing a functional group to give heterocyclic compounds in most cases. It makes the investigations on the functionalized allenes, more specifically in studying their reactions with electrophilic reagents, quite an interesting and topical task.

Recently, we developed the electrophilic cyclization reactions of 1- and 3-vinylallenyl sulfoxides[7] and sulfones.[8] In all the cases, the electrophilic atom has been introduced to the central carbon atom of the allene moiety and the reactions proceeded with participation of the allenic and/or 1,3-dienic part of the vinylallenic system with neighboring group participation of sulfinyl (sulfonyl) and/or vinylic group.[7,8]

Literature data on the electrophilic addition reactions to phosphorylated allenes (phosphonates, phosphinates, and phosphine oxides) show that various five-membered heterocyclizations proceed in most cases.[4,6,9–12] On the other hand, the reactions of the 1,2,4- and 1,3,4-alkatrienephosphonates with electrophiles lead to the synthesis of various heterocyclic compounds. For example, the halogenation reactions afford the 3- or 5-vinyl-substituted 2,5-dihydro-1,2-oxaphospholes,[13,16] while the interaction with sulfenyl[14,16] and selenenyl[15,16] chlorides gives the thiophene- or selenophene-2- or 3-phosphonates.

There are methods[17] for the synthesis of phosphorus-containing allenes (phosphonates,[18] phosphinates,[19] and phosphine oxides[20]) including reactions of α-alkynols with chloride-containing derivatives of phosphorus acids followed by [2,3]-sigmatropic rearrangement.

As a part of our long-standing program on the synthesis and cyclization reactions of sulfur- and phosphorus-functionalized vinylallenes, we now report the results on the synthesis of diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide and the reactions with some electrophilic reagents for study of the electrophilic cyclization reactions.

DISCUSSION

Since its discovery five decades ago,[18a,19a,19b] the reversible interconversion of propargylic phosphites, phosphonites, and phosphinites to allenyl phosphonates, phosphinates, and phosphine oxides has become one of the most studied and

synthetically useful [2,3]-sigmatropic rearrangements. Numerous synthetic applications of the rearrangement have been reported, including its use in the synthesis of allenic steroids as substrate-induced inactivation of aromatase,[21a] in the efficient synthesis of (2*R*)-2-amino-5-phosphonopentanoic acid (AP5) as a powerful and selective N-methyl-*D*-aspartate (NM*D*A) antagonist,[21b] in the preparation of the phosphonate analogs of phosphatidyl derivatives,[21c,21d] and in the synthesis of new acyclic analogs of nucleotides containing a purine or pyrimidine moiety and an allenic skeleton.[21e,21f]

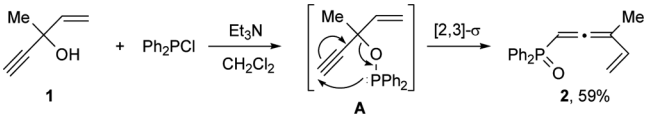
Our strategy for the synthesis of diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2**, using our experience on the preparation of the vinylallenyl sulfoxides[7] and sulfones,[8] relies on the well-precedented [2,3]-sigmatropic shift of propargylic phosphinites to allenyl phosphine oxides.[20]

Diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2** can be readily prepared via an atom-economical [2,3]-sigmatropic rearrangement of the mediated alkenynyl phosphinite **A** formed in situ by reaction of the 3-methylpent-1-en-4-yn-3-ol **1** with diphenylchlorophosphine in the presence of triethylamine according to Scheme 1.

After a conventional workup, the resulting compound **2** was isolated by column chromatography as a pale yellow oil and identified by ^{1}H and ^{13}C NMR and infrared (IR) spectra as well as by elemental analysis.

The vinylallenyl phosphine oxide **2** isolated in preparative amounts allowed us to study its chemical behavior in the reactions with electrophilic reagents. From general considerations as well as from the literature data on the electrophilic addition reactions[22] to phosphorylated allenes,[4] 1,2,4- and 1,3,4-alkatrienephosphonates,[13–16] and vinylallenyl sulfoxides[7] and sulfones,[8] the following pathways of the reactions could be assumed:

i. Attack of the reagent on the C^2-C^3 double bond with formation of 2,3-adduct;
ii. Attack of the reagent on the C^2-C^3 double bond with formation of 1,3-alkadienic system and preparation of 2,5-adduct;
iii. Attack of the reagent on the C^2-C^3 double bond of the trienic system and following neighboring group participation of the internal nucleophile (phosphoryl group) and ring closure to five-membered cyclic compound;
iv. Attack of the reagent on the C^2-C^3 double bond of the trienic system and following neighboring group participation of the vinylic double bond and ring closure to cyclic compound;
v. Attack of the reagent on the C^1-C^2 double bond with formation of 1,2-adduct; and
vi. Elimination reactions after realization of some of the above mentioned pathways (i–v).



Scheme 1. Synthesis of diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2**.

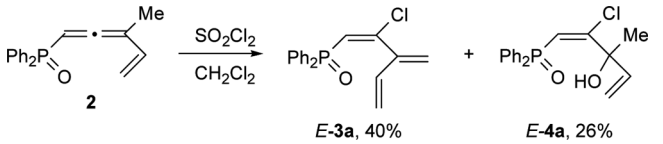
We initially examined the halogenation reaction of the diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2** with sulfuryl chloride. According to our previous experimental results on the electrophilic cyclization reactions of functionalized vinylallenes,[7,8] dichloromethane was a good solvent for electrophilic addition reactions of allenes. When CH_2Cl_2 was used as the solvent, the diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2** reacted with SO_2Cl_2 at -20 °C to give a mixture of (1*E*)-2-chloro-3-methylene-penta-1,4-dienyl diphenyl phosphine oxide **3a** and (1*E*)-2-chloro-1-(diphenylphosphoryl)-3-methyl-penta-1,4-dien-3-ol **4a** in the ratio of **3a**/**4a** being 1.5/1 in 66% yield, according to the reaction sequence outlined in Scheme 2.

The resulting compounds *E*-**3a** and *E*-**4a** were isolated by column chromatography as oils and identified by ^{1}H and ^{13}C NMR and IR spectra as well as by elemental analysis.

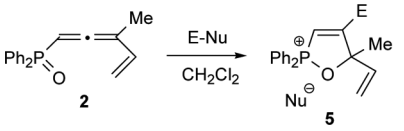
Obviously, the hydroxyl group in *E*-**4a** was formed from the water in the reaction media, as it was shown by Ma and coworkers in the iodohydroxylation,[9] fluorohydroxylation,[10] and selenohydroxylation[11] reactions of allenyl phophine oxides with iodine, selectfluor, and benzeneselanyl chloride. A mechanistic rationale for the formation of the trienyl phosphine oxide *E*-**3a** in the elimination reaction of hydrogen chloride and the 3-hydroxy-1,4-dienyl phosphine oxide *E*-**4a** in hydrolysis reaction would appear not to be straightforward. The result reported previously can be considered in terms of the following two assumptions:

i. Intermediate formation of the C^3-carbenium ion and following elimination of hydrogen chloride after an attack of chloride anion on the methyl group to give *E*-**3a** as has been shown by Horner and Binder[23] and Braverman and Reisman[24] in the case of halogenation of allenyl sulfoxides and sulfones or following water addition to C^3 atom of the carbenium ion to afford *E*-**4a**; and
ii. Deprotonation to give *E*-**3a** after an attack of chloride anion on the methyl group and the C^5-O bond cleavage or water molecule attacks the positively charged phosphorus atom to cleave the P-O bond, forming *E*-**4a**, both in the stage of the in situ–generated cyclic 2,5-dihydro-1,2-oxaphosphol-2-ium chloride as Ma and coworkers[9–11] and Saalfrank and coworkers[25] supposed in the reactions of the allenyl phosphine oxides with electrophilic reagents.

The results reported confirm our second assumption that the reaction of vinylallenyl phosphine oxide **2** with sulfuryl chloride leading to the formation of a mixture of *E*-**3a** and *E*-**4a** probably proceeds through the cyclic phosphonium chloride, which corroborates our results on the reactions of the vinylallenyl phosphine oxide **2** with bromine and iodine (Scheme 3), sulfanyl (Scheme 4), and selanyl (Scheme 5) chlorides.



Scheme 2. Chlorination reaction of diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2** with sulfuryl chloride.



5	E	Nu	Yield, %
b	Br	Br	75
c	I	I	68

Scheme 3. Bromination and iodination reactions of diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2**.

Moreover, the *E*-configuration of the triene *E*-**3a** and the diene *E*-**4a** was assigned on the base of the chemical shift values[26] of the olefinic proton at C^1 atom and of the C^1 atom in the ^1H and ^{13}C NMR spectra. In addition, the intermediate formation of the cyclic 2,5-dihydro-1,2-oxaphosphol-2-ium chloride predetermines the configuration of the products *E*-**3a** and *E*-**4a**.

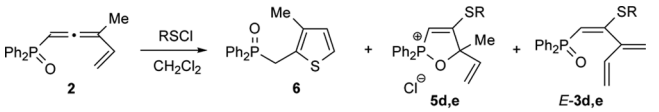
In contrast to the chlorination, the bromination and iodination reactions of the alkatrienyl phosphine oxide **2** were carried out with five-membered heterocyclization of the allenic system of double bonds bearing a phosphoryl group (C=C = C-P=O) to give 2,5-dihydro-1,2-oxaphosphol-2-ium bromide **5b** and iodide **5c** in 75% and 68% yields as shown in Scheme 3.

The results reported in Scheme 3 confirm our second assumption that the reaction of the vinylallene **3** with sulfuryl chloride probably proceeds through the 1,2-oxaphosphol-2-ium chloride. Another confirmation for that is the next results on the electrophilic reactions of **2** with sulfanyl and selanyl chlorides.

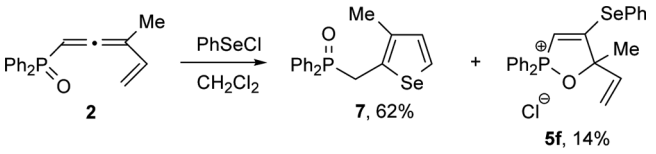
Surprisingly, reaction of the 1,2,4-trienyl phosphine oxide **2** with methane- and benzenesulfanyl chlorides proceeds with two types of electrophilic cyclization by neighboring group participation of both the vinylic double bond and the phosphine oxide group to give mixtures of the 2-(diphenylphosphorylmethyl)-thiophene **6**, the 4-methyl(phenyl)sulfanyl-2,5-dihydro-1,2-oxaphosphol-2-ium chlorides **5d**, and **e**, and their dehydrochlorination products—the (1*E*)-3-methylene-2-methyl(phenyl)-sulfanyl-penta-1,4-dienyl diphenyl phosphine oxides **3d**, and **e** in 75–78% overall yields according to the sequence outlined in Scheme 4.

The products **6**, **5d**, and **5e** and *E*-**3d**, and **e** were isolated by column chromatography as oils and identified by ^1H and ^{13}C NMR and IR spectra as well as by elemental analysis.

In a similar way, a ca. 4.4:1 mixture of the 2-(diphenylphosphorylmethyl)-selenophene **7** and the 4-phenylselanyl-2,5-dihydro-1,2-oxaphosphol-2-ium chloride **5f** was obtained with 76% overall yield from the reaction of the vinylallenyl phosphine oxide **2** with benzeneselanyl chloride in dry dichloromethane at −10 °C as outlined in Scheme 5.



Scheme 4. Sulfanylation reaction of diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2**.



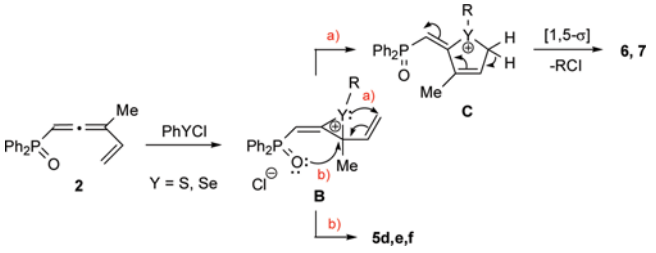
Scheme 5. Selanylation reaction of diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2**.

Resulting selenophene **7** and oxaphosphole **5f** were isolated by column chromatography and identified by ^{1}H and ^{13}C NMR and IR spectra as well as by elemental analysis. The obtained compounds **7** and **5f** contain the isotope ^{77}Se, which is magnetically active and interacts with other nuclei. This interaction becomes evident with the protons and carbons of the neighboring groups, which exhibit symmetric satelite signals of the main signal in the ^{1}H and ^{13}C NMR spectra.[27]

On the basis of previous results,[7,8] a plausible is proposed (Scheme 6). The initial act is the attack of electrophilic sulfur or selenium on the most nucleophilic atom of the trienic system of π bonds (C^2) with the formation of the cyclic onium (thiiranium or seleniranium) ions **B** after an attack on the relatively electron-rich C^2-C^3 double bond. The ions **B** are in the plane of the π bond of the vinyl group (*s-cis* conformation), and for this reason, **B** are easily transformed into the more stable five-membered cyclic ions **C**. Further, the ions **C** undergo elimination of methyl or phenyl chloride, [1,5]-prototropic shift, and aromatization to give the thiophene **6** or selenophene **7**. The five-membered cyclic phosphonium chlorides **5d–f** is formed via neighboring group participation of the oxygen atom of the diphenyl phosphine oxide functionality in the stage of ions **B** formation.

The simultaneous realization of the both heterocyclization processes is connected with introduction of the allenic and 1,3-dienic parts of the trienic system into the reaction course. This fact is obviously a result the ability of the sulfur and selenium to form cyclic ions,[28] which are further transformed into five-membered heterocyclic compounds.

In terms of reaction mechanism of the trienyl phosphine oxides *E*-**3a**, **d**, and **e** and the 3-hydroxy-1,4-dienyl phosphine oxide *E*-**4a** formation, we carried out the elimination and hydrolysis reactions of the cyclic 2,5-dihydro-1,2-oxaphosphol-2-ium halides **5b–f**. Heating at reflux of the cyclic phosphonium salts **5** in 1,2-dichloroethane for 3 h provoked elimination of hydrogen halide and C^5-O bond cleavage in



Scheme 6. Proposed mechanism of sulfanylation and selanylation reactions. (Figure is provided in color online.)

the ring with generation of the 3-methylene-penta-1,4-dienyl phosphine oxides *E*-**3b–e** in good yield (64–68%) as shown in Scheme 7.

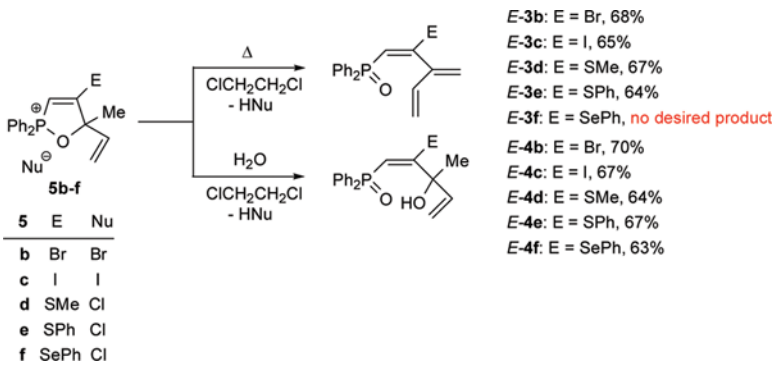
The attempts at an elimination reaction of hydrogen chloride of the 4-phenylselanyl-2,5-dihydro-1,2-oxaphosphol-2-ium chloride **5f** were not successful. In all cases, no traces of the expected 1,4-dienyl phosphine oxide **3f** were detected. Instead complex mixtures of decomposed products were obtained.

The hydrolysis reaction of the 2,5-dihydro-1,2-oxaphosphol-2-ium halides **5b–f** occurs with the water molecule attack at the positively charged phosphorus atom to cleave the P-O bond,[9–11] which results in the formation of final (1*E*)-1-(diphenylphosphoryl)-3-methyl-penta-1,4-dien-3-ols **4b–f** in 63–70% yields, according to the sequence outlined in Scheme 7.

In conclusion, we note the following points from this investigation:

i. Diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2** can be readily prepared via an atom economical [2,3]-sigmatropic rearrangement of the mediated alkenynyl phosphinite formed in situ by reaction of 3-methylpent-1-en-4-yn-3-ol with diphenylchlorophosphine.
ii. Electrophilic cyclization reactions of the vinylallenyl phosphine oxide **2** were investigated as it was established that the reactions proceeded with formation of various heterocyclic and/or highly unsaturated compounds with participation of the allenic and/or 1,3-dienic part of the vinylallenic system with neighboring participation of phosphoryl and/or vinylic group.
iii. Elimination and hydrolysis reactions of the cyclic 2,5-dihydro-1,2-oxaphosphol-2-ium salts **5b–f** formed proceed with the C^5-O or P-O bond cleavage in the ring with generation of the highly unsaturated phosphine oxides *E*-**3b–e** or *E*-**4b–f**.
iv. The diphenyl 3-methyl-penta-1,2,4-trienyl phosphine oxide **2** is a versatile synthone for heterocyclic and unsaturated compounds in organic synthesis.

Results of an initial investigation of the physiological activity of the compounds prepared were encouraging and the activity of selected compounds is now under investigation. A continuation of these studies toward the synthesis and



Scheme 7. Opening ring reactions of 2,5-dihydro-1,2-oxaphosphol-2-ium salts **5b-f**. (Figure is provided in color online.)

electrophilic cyclization reactions of other functionalized vinylallenes is currently in progress in our laboratory.

EXPERIMENTAL

Synthesis of 3-Methylpenta-1,2,4-trienyl Diphenyl Phosphine Oxide 2

A solution of freshly diphenylchlorophosphine (6.62 g, 30 mmol) in dry dichloromethane (20 mL) was added dropwise with stirring to a solution of 3-methylpent-1-en-4-yn-3-ol **1** (3.36 g, 30 mmol) and triethylamine (3.34 g, 33 mmol) in dry dichloromethane (50 mL) at −70 °C. The reaction mixture was stirred for 1 h at the same temperature and for 3 h at rt, washed with water (50 ml) and 2 N HCl, and extracted with ether, and the extract was washed with saturated NaCl and dried over anhydrous sodium sulfate. Evaporation yielded the crude product **2**, which was purified by column chromatography on silica gel. Pale yellow oil, yield: 59%.

Electrophilic Cyclization Reactions of the 3-Methylpenta-1,2,4-trienyl Diphenyl Phosphine Oxide 2

A solution of electrophilic reagent (sulfuryl chloride, bromine, iodine, methanesufanyl chloride, benzenesulfanyl chloride, and benzeneselanyl chloride) (10 mmol) in dry dichloromethane (10 mL) was added dropwise with stirring to a solution of triene **2** (2.80 g, 10 mmol) in dry dichloromethane (20 mL) at −20 °C. The reaction mixture was stirred for 1 h at the same temperature and for 3 h at rt. The solvent was removed using a rotatory evaporator, and the residue was purified by column chromatography on silica gel (Kieselgel Merck 60 F_{254}) with ethyl acetate / heptane.

Elimination Reaction of the 2,2-Diphenyl-5-vinyl-5-methyl-2,5-dihydro-1,2-oxaphosphol-2-ium Salts 5b–f

A solution of the cyclic phosphonium salts **5b–f** (5 mmol) in dry 1,2-dichloromethane (10 mL) was refluxed with stirring for 3 h. The reaction mixture was stirred for 1 h at rt and then extracted with ether, and the extract was washed with saturated NaCl and dried over anhydrous sodium sulfate. Evaporation yielded the crude product, which was purified by column chromatography on silica gel with ethyl acetate/heptane as eluents.

Elimination Reaction of the 2,2-Diphenyl-5-vinyl-5-methyl-2,5-dihydro-1,2-oxaphosphol-2-ium Salts 5b–f

A solution of the cyclic phosphonium salts **5b–f** (5 mmol) in dry 1,2-dichloromethane (10 mL) was refluxed with stirring for 3 h. The reaction mixture was stirred for 1 h at rt and then extracted with ether, and the extract was washed with saturated NaCl and dried over anhydrous sodium sulfate. Evaporation yielded the crude product, which was purified by column chromatography on silica gel with ethyl acetate/heptane as eluents.

Supplementary Material Available Online

Method of analysis, starting materials, and full spectroscopic and characterization data including ^{1}H and ^{13}C NMR and IR spectral data and elemental analysis for all new compounds and literature references to these data for known compounds are listed.

ACKNOWLEDGMENTS

Support from the Research Fund of the Konstantin Preslavsky University of Shumen (Projects No. RD-05-367 / 2010 and No. RD-05-137 / 2011) is acknowledged. Special thanks to Hasan Hasanov for the technical help in the chromatographical separations.

REFERENCES

1. (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; Vols. 1–3 (c) Pasto, D. J. Tetrahedron 1984, 40, 2805–2827; (d) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley & Sons: New York, 1988; (e) Zimmer, R. Synthesis 1993, 165–178; (f) Elsevier, C. J. *Methods of Organic Chemistry*; R.W. Helmchen, J. Mulzer, and E. Schaumann (Eds.); Thieme: Stuttgart, 1995; Vol. E21a, pp. 537–566; (g) Krause, N.; Hashmi, A. S. K. (Eds.) *Modern Allene Chemistry*; Wiley-VCH: Weinheim, 2004; Vols. 1 & 2; (h) Brummond, K. M.; DeForrest, J. E. Synthesis 2007, 795–818.
2. (a) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev*. **2002**, *31*, 12–21; (b) Ma, S. *Aldrichim. Acta* **2007**, *40*, 91–102; (c) Hassan, H. H. A. M. *Curr. Org. Synth.* **2007**, *4*, 413–439; (d) Back, T. G.; Clary, K. N.; Gao, D. *Chem. Rev.* **2010**, *110*, 4498–4553.
3. (a) de la Mare, P. B. D.; Bolton, R. *Electrophilic Addition to Unsaturated Systems*; Elsevior: Amsterdam, 1966; pp. 250–266; (b) Caserio, M. C. *Selectivity in Addition Reactions of Allenes in Selective Organic Transformations*; B. S. Thyagarajan, (Ed.); John Wiley & Sons: New York, 1970; pp. 239–299; (c) de la Mare, P. B. D.; Bolton, R. *Electrophilic Addition to Unsaturated Systems*; Elsevior: Amsterdam, 1982; pp. 317–325; (d) Jacobs, T. L. *Electrophilic Addition to Allenes in the Chemistry of the Allenes*; S. R. Landor (Ed.); Academic press: New York, 1982; Vol. 2, pp. 417–510; (e) Smadja, W. Chem. Rev. 1983, 83, 263–320; (f) Ma, S. *Ionic Addition to Allenes in Modern Allene Chemistry*; N. Krause and A. S. K. Hashmi (Eds.); Wiley-VCH: Weinheim, 2004; Vol. 2, pp. 595–699.
4. (a) Angelov, C. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1983**, *15*, 177–193; (b) Khusainova, N. G.; Pudovik, A. N. *Russ. Chem. Rev.* **1987**, *56*, 564–578; (c) Alabugin, I. V.; Brel, V. K. *Russ. Chem. Rev.* **1997**, *66*, 205–224.
5. Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679–1688.
6. Brel, V. K. *Heteroatom Chem.* **2006**, *17*, 547–556.
7. (a) Christov, V. C.; Ivanov, I. K. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 2445–2454; (b) Christov, V. C.; Ivanov, I. K. *Sulfur Lett.* **2002**, *25*, 191–198.
8. (a) Christov, V. C.; Ivanov, I. K. *Heterocycl. Commun.* **2003**, *9*, 629–634; (b) Christov, V. C.; Ivanov, I. K. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 1681–1690.
9. Guo, H.; Qian, R.; Guo, Y.; Ma, S. *J. Org. Chem.* **2008**, *73*, 7934–7938.
10. He, G.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 8035–8042.
11. He, G.; Guo, H.; Qian, R.; Guo, Y.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 4877–4889.
12. Yuan, J.; Ruan, X.; Yang, Y.; Huang, X. *Synlett* **2007**, 2871–2874.

13. (a) Angelov, C. M.; Kirilov, M.; Ionin, B. I.; Petrov, A. A. *J. Gen. Chem.* **1979**, *49*, 2225–2230; (b) Angelov, C. M.; Stoianov, N. M.; Ionin, B. I. *J. Gen. Chem.* **1982**, *52*, 178–181; (c) Angelov, C. M., Christov, C. Z. *Synthesis* **1984**, 664–667.
14. (a) Angelov, C. M.; Kirilov, M.; Vachkov, K. V.; Spassov, S. L. *Tetrahedron Lett.* **1980**, *21*, 3507–3508; (b) Angelov, C. M.; Vachkov, K. V. *Tetrahedron Lett.* **1981**, *22*, 2517–2520.
15. (a) Angelov, C. M.; Christov, C. Z. *Phosphorus, Sulfur Silicon Relat. Elem.* **1983**, *15*, 373–375; (b) Tancheva, T. N.; Angelov, C. M.; Mondeshka, D. M. *Heterocycles* **1985**, *22*, 843–852.
16. Angelov, C. M.; Enchev, D. D.; Kirilov, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1988**, *20*, 35–39
17. (a) Mark, V. *The Uncatalyzed Rearrangements of Tervalent Phosphorus Esters in Selective Organic Transformations*; B. S. Thyagarajan (Ed.); John Wiley & Sons: New York, 1970; pp. 319–437; (b) Landor, P. D. *The Chemistry of the Allenes*; S. R. Landor (Ed.); Academic Press: New York, 1982; Vol. 1, pp. 174–178; (d) Saalfrank, R. W.; Lurz, C.-J. *Methoden der Organischen Chemie*; H. Kropf, and E. Scheumann (Eds.); Thieme: Stuttgart, 1993; pp. 2959–3102; (e) Hashmi, A. S. K. *Synthesis of Allenes in Modern Allene Chemistry*; N. Krause, and A. S. K. Hashmi (Eds.); Wiley-VCH: Weinheim, 2004; Vol. 1, pp. 3–50.
18. (a) Pudovik, A. N.; Aladjeva, I. M. *Russ. J. Gen. Chem.* **1963**, *33*, 700–706; (b) Macomber, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 3072–3075; (c) Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1991**, *56*, 1003–1013; (d) Cai, B.; Blackburn, G. M. *Synth. Commun.* **1997**, *27*, 3943–3949. (e) Saalfrank, R. W.; Haubner, M.; Deutscher, C.; Bauer, U. *Eur. J. Org. Chem.* **1999**, 2367–2372.
19. (a) Boiselle, A. P.; Meinhardt, N. A. *J. Org. Chem.* **1962**, *27*, 1828–1833; (b) Mark, V. *Tetrahedron Lett.* **1962**, 281–284; (c) Sevin, A.; Chodkiewicz, W. *Bull. Soc. Chim. Fr.* **1969**, 4016–4021; (d) Ignatev, V. M.; Timofeeva, T. N.; Ionin, B. I.; Petrov, A. A. *Russ. J. Gen. Chem.* **1969**, *39*, 1567–1572.
20. (a) Nicolaou, K. C.; Maligres, P.; Shin, J.; de Leon, E.; Rideout, D. *J. Am. Chem. Soc.* **1990**, *112*, 7825–7826; (b) Curfin, M. L.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 5278–5287; (c) Grissom, J. W.; Huang, D. *Angew. Chem. Int. Ed.* **1995**, *34*, 2037–2039; (d) Darcel, C.; Bruneau, C.; Dixneuf, P. H. *Synthesis* **1996**, 711–714; (e) de Frutos, O.; Echavarren, A. M. *Tetrahedron Lett.* **1997**, *38*, 7941–7943; (f) Schmittel, M.; Steffen, J.-P.; Maywald, M.; Engels, B.; Helten, H.; Musch, P. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1331–1342.
21. (a) Metcalf, B. W.; Wright, C. L.; Burkhart, J. P.; Johnston, J. O. *J. Am. Chem. Soc.* **1981**, *103*, 3221–3222; (b) Muller, M.; Mann, A.; Taddei, M. *Tetrahedron Lett.* **1993**, *34*, 3289; (c) Brel, V. K.; Stang, P. J. *Eur. J. Org. Chem.* **2003**, 224–229; (d) Brel, V. K. *Synthesis* **2001**, 1539–1545; (e) Brel, V. K.; Belsky, V. K.; Stash, A. I.; Zvodnik, V. E.; Stang, P. J. *Org. Biomol. Chem.* **2003**, *1*, 4220–4226; (f) Brel, V. K.; Belsky, V. K.; Stash, A. I.; Zvodnik, V. E.; Stang, P. J. *Eur. J. Org. Chem.* **2005**, 512–521.
22. Egenburg, I. Z. *Russ. Chem. Rev.* **1978**, *47*, 470–485
23. Horner, L.; Binder, V. *Liebigs Ann. Chem.* **1972**, *757*, 33–68.
24. Braverman, S.; Reisman, D. *Tetrahedron Lett.* **1977**, *18*, 1753–1756.
25. Saalfrank, R. W.; Welch, A.; Haubner, M.; Bauer, U. *Liebigs Ann. Chem.* **1996**, 171–181.
26. Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Tabellen zur Structuraufklarung organischer Verbindungen mit spectrockopischen Methoden*; Springer-Verlag: Berlin,1981.
27. Simonin, M. P.; Pauet, M. J.; Gense, J. M.; Paumier, C. *Org. Magn. Resonance* **1976**, *8*, 508–512.
28. (a) Capozzi, G.; Modena, G.; Pasquato, L. *The Chemistry of Sulphenyl Halides and Sulphenamides*; S. Patai (Ed.); John Wiley & Sons: Chichester, 1990; Ch. 10; (b) Schmid, G. H.; Garratt, D. G. *Tetrahedron Lett*. **1975**, *16*, 3991–3994.