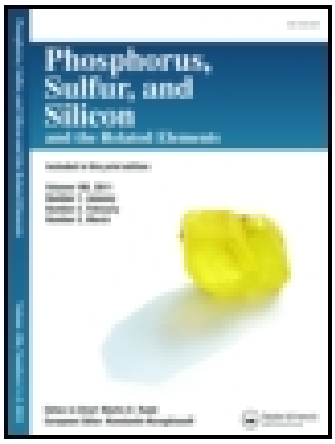

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Alkatrienyl Sulfoxides and Sulfones. Part I. 3-Methyl-1,2,4-pentatrienyl Phenyl Sulfoxide-Synthesis and Electrophile-Induced Cyclization Reactions

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ALKATRIENYL SULFOXIDES AND SULFONES. PART I. 3-METHYL-1,2,4-PENTATRIENYL PHENYL SULFOXIDE-SYNTHESIS AND ELECTROPHILE-INDUCED CYCLIZATION REACTIONS

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*A method for the synthesis of the 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide **3** by [2,3]-sigmatropic rearrangement of the 3-methyl-1-penten-4-yn-3-yl benzenesulfenate **2**, formed in the reaction of the 3-methyl-1-pentene-4-yn-2-ol **1** with phenylsulfenyl chloride has been created. Possibilities and restrictions of the five-membered heterocyclization in electrophile-induced reactions leading to the synthesis of the 5H-1,2-oxathiol-2-ium salts **5**, **7**, and **8** have been explored. Chlorination of the sulfoxide **2** proceeded with formation of the (E)-2-chloro-3-methylene-1,4-pentadienyl phenyl sulfoxide **4**, while the bromination afforded the 4-bromo-5H-1,2-oxathiol-2-ium bromide **5**, which after reflux in 1,2-dichloroethane eliminated hydrogen bromide and was transformed into the (E)-2-bromo-3-methylene-1,4-pentadienyl phenyl sulfoxide **6**.*

Keywords: 2-Halogeno-3-methylene-1,4-pentadienyl phenyl sulfoxide; 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide; *5H*-1,2-oxathiol-2-ium salts; electrophile-induced cyclic reactions; synthesis

INTRODUCTION

One of the characteristic reactions of the 1,2-alkadienes (allenes) are the electrophilic addition reactions in which the addition products of the reagent to one bond or to double bonds of the allenic system are usually obtained.[1–5] Functionalized allenes are very interesting substrates

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as a material of choice to study the addition reactions on the carbon-carbon double bonds.[3,4] 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[3,4] 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.

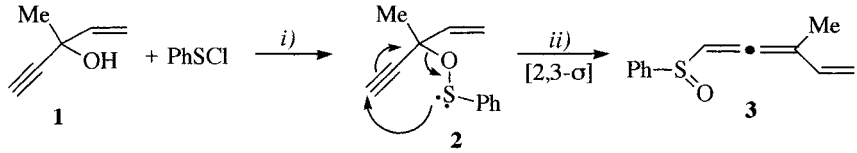
Literature data on the electrophilic addition reactions to sulfur-containing allenes (sulfoxides, sulfinates, and sulfones) shows that various five-membered heterocyclizations proceed in most cases.[7,9,14–16] On the other hand, the reactions of the phosphorylated 1,2,4- and 1,3,4-alkatrienes with electrophiles lead to the synthesis of various heterocyclic compounds depending on the kind of the electrophilic reagent as well as on the position of the vinylic group. For example, the halogenation reactions afford the 3- or 5-vinyl-substituted 2,5-dihydro-1,2-oxaphospholes,[17–20] while the reactions with sulfenyl[20–22] and selenenyl[19,20,23,24] chlorides give the thiophene- or selenophene-2- or 3-phosphonates.

There are methods[6–13] for the synthesis of sulfur-containing allenes (sulfoxides,[6–8] sulfinates,[9] sulfinamides,[10,11] and sulfones),[12,13] including reactions of α-alkynols with sulfenyl or sulfinyl chlorides followed by [2,3]-sigmatropic rearrangement. The synthetic utility of the remarkable and efficient [2,3]-sigmatropic rearrangement of propargylic sulfenates has been further demostrated, by W. H. Okamura and coworkers, in a variety of preparations and interesting reactions of allenyl sulfoxides,[25–28] including the preparation of vinylallenes[25–30] which are useful intermediates in organic synthesis in general[29] and natural polyenes, such as Vitamins A and D, in particular.[30] Electrophilic addition reactions to alkatrienyl sulfoxides and sulfones have not been investigated to date.

As part of our general program on the synthesis and cyclization reactions of highly unsaturated compounds, we decided to prepare a series of alkatrienyl sulfoxides and sulfones so as to evaluate their chemical reactivity with respect to make a study of the possibilities and restrictions of the electrophile-induced cyclization reactions. The article documents the results on the synthesis and the reactions with some electrophilic reagents (sulfuryl chloride, bromine, methyl- and phenylsulfenyl chlorides and phenylselenenyl chloride) of 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide as an initial substrate for study of the electrophile-induced heterocyclization reactions.

RESULTS AND DISCUSSION

Since its discovery three decades ago,[6] the reversible interconversion of propargylic sulfenates to allenyl sulfoxides has become one of the most studied and synthetically useful [2,3]-sigmatropic rearrangement known. Numerous synthetic applications of the rearrangement have been reported, including its use in the total synthesis of a variety of natural products such as steroids, prostaglandins, and leukotrienes.[14] Our strategy for the synthesis of 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide **3** relies on the well-precedented [2,3]-sigmatropic shift of propargylic sulfenates to α-allenic sulfoxides. This compound was prepared in 85% yield by reaction of freshly distilled phenylsulfenyl chloride with 3-methyl-1-pentene-4-yn-3-ol **1** in the presence of triethylamine and followed by [2,3]-sigmatropic rearrangement of the transient intermediate 3-methyl-1-pentene-4-yn-3-yl benzenesulfenate **2** according to Scheme 1.

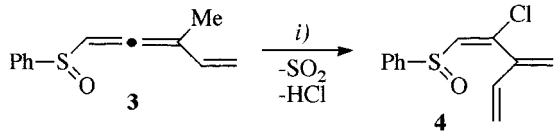


SCHEME 1 Reagents and conditions: 1) PhSCl, Et_3N dry ether, $-40^\circ C$; 2) dry ether, rt, 3 h.

After a conventional work-up, the resulting compound **3** was isolated by column chromatography as a light yellow oil and identified by ^1H and ^{13}C NMR and IR spectra as well as elemental analysis.

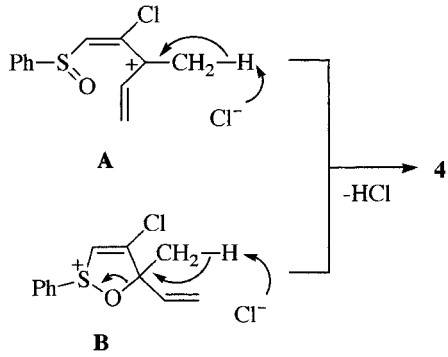
The alkatrienyl sulfoxide **3** isolated in preparative amount allowed us to study its chemical behavior in the reactions with electrophilic reagents. From general considerations as well as from the literature data on the electrophilic addition reactions to sulfur-containing allenes[7,9,14–16] and to phosphorylated alkatrienes,[17–24] the following pathways of the reactions could be assumed: (1) attack of the reagent on the C^2—C^3 double bond of the allenic system followed by neighboring group participation of the internal nucleophile (sulfoxide group) and ring closure to the five-membered cyclic compound; (2) attack of the reagent on the C^2—C^3 double bond with formation of the 2,3-adduct; (3) attack of the reagent on the C^2—C^3 double bond with formation of the 1,3-alkadienic system and preparation of the 2,5-adduct; (4) attack of the reagent on the C^1—C^2 double bond with formation of the 2,1-adduct; and (5) elimination reactions after realization of some of above mentioned pathways (1–4).

We established that reaction of the trienyl sulfoxides **3** with sulfuryl chloride in dichloromethane proceeded with formation of 2-chloro-3-methylene-1,4-pentadienyl phenyl sulfoxide **4** in 62% yield, according to the following reaction sequence outlined in Scheme 2.



SCHEME 2 Reagents and conditions: 1) SO_2Cl_2, dry CH_2Cl_2, $-10^{\circ}C$, rt, 3 h.

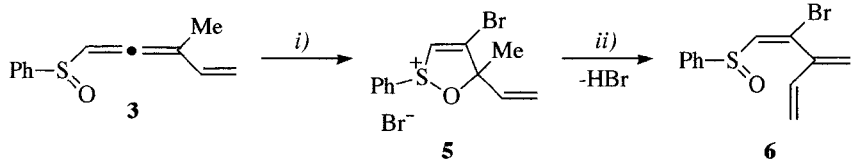
The resulting conjugated sulfoxide **4** was isolated by column chromatography as a yellow oil and identified by ^1H and ^{13}C NMR and IR spectra as well as elemental analysis. A mechanistic rationale for the formation of the sulfoxide **4** by an elimination reaction of hydrogen chloride would appear not to be straightforward. The result reported above can be considered in terms of the following two assumptions (Scheme 3): (1) intermediate formation of the stabilized carbenium ion **A** followed by elimination of hydrogen chloride after an attach of the chloride anion on the methyl group at C^3-atom as has been shown by S. Braverman and D. Reisman[9] in the case of halogenation of allenyl sulfones; and (2) deprotonation in the stage of the in situ generated cyclic sulfonium chloride **B** as shown by L. Horner and V. Binder[7] in the reaction of allenyl sulfoxides with electrophilic reagents and which was in corroboration of our results on the reactions of the alkatrienyl sulfoxide **3** with bromine, sulfenyl, and selenenyl chlorides.



SCHEME 3

In contrast to the chlorination, the bromination reaction of the alkatrienyl sulfoxide **3** let to five-membered heterocyclization of the allenic system of double bonds bearing a sulfoxide group (C=C=C–S=O) to give the 4-bromo-5-methyl-2-phenyl-5-vinyl-*5H*-1,2-oxathiol-2-ium

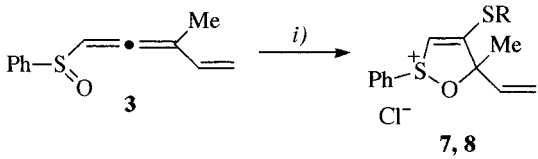
bromide **5** in 87% yield as shown in Scheme 4. Heating at reflux of the cyclic sulfonium bromide **5** in 1,2-dichloroethane for 1.5 h provoked elimination of hydrogen bromide and C^5—O bond cleavage in the ring with generation of the 2-bromo-3-methylene-1,4-pentadienyl phenyl sulfoxide **6** in good yield (61%).



SCHEME 4 Reagents and conditions: 1) Br_2, dry CH_2Cl_2, −10°C, rt, 3 h; 2) dry $ClCH_2CH_2Cl$, reflux, 1.5 h.

The results reported in the Scheme 4 confirm our second assumption in Scheme 3 that the reaction of alkatrienyl sulfoxide **3** with sulfuryl chloride gives 2-chloro-3-methylene-1,4-pentadienyl phenyl sulfoxide **4** probably proceeding through the 1,2-oxathiol-2-ium chloride **B**. Another confirmation for that are the next results on the reactions of the alkatrienyl sulfoxide **3** with sulfenyl and selenenyl chlorides. Moreover, the configuration of the prepared 2-halogeno-3-methylene-1,4-pentadienyl phenyl sulfoxides **4** and **6** is most likely (*E*). The (*E*) stereochemistry could be based upon the chemical shift value of the olefinic proton at the C^1 atom. Although it was anticipated that the olefinic proton of the (*E*)-isomers would be observed in the ^{1}H NMR spectrum upfield from the corresponding proton of the (*Z*)-isomers, with the chemical shift value (s, δ 6.58 for **4** and s, 6.85 ppm for **6**) alone we cannot determine whether the 1,4-dienes **4** and **6** are (*E*) or (*Z*) isomers. Nevertheless, the intermediate formation of the cyclic sulfonium salts **B** and **5** predetermines the (*E*) configuration of the 1,4-alkadienyl sulfoxides **4** and **6**.

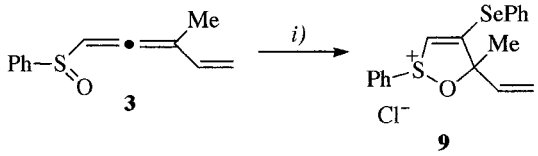
Reaction of 1,2,4-alkatrienyl sulfoxide **3** with methyl- and phenylsulfenyl chlorides were also carried out with heterocyclization to give the 5-methyl-2-phenyl-4-methyl(phenyl)thio-5-vinyl-*5H*-1,2-oxathiol-2-ium chlorides **7** and **8** in 74 and 69% yields as shown in Scheme 5.



R = Me (**7**), Ph (**8**).

SCHEME 5 Reagents and conditions: 1) RSCl, dry CH_2Cl_2, −10°C, rt, 4 h.

In a similar way, the 5-methyl-2-phenyl-4-phenylseleno-5-vinyl-*5H*-1,2-oxathiol-2-ium chloride **9** was obtained with 62% yield in the interaction of the alkatrienyl sulfoxide **3** with phenylselenenyl chloride in dry dichloromethane at −10°C, according to the following reaction sequence outlined in Scheme 6.



SCHEME 6 Reagents and conditions: 1) PhSeCl, dry CH_2Cl_2, −10°C, rt, 4 h.

The resulting cyclic sulfonium chlorides **7–9** were isolated by column chromatography as yellow oils and identified by ^1H and ^{13}C NMR and IR spectra as well as elemental analysis. The obtained compound **9** contains the isotope ^{77}Se which is magnetically active and interacts with other nuclei. This interaction becomes evident with the protons of the neighboring groups which exhibit symmetric satelite signals of the main signal in the ^1H NMR spectra.

The attempts to eliminate hydrogen chloride of the cyclic sulfonium chlorides **7–9** by heating at reflux in different solvents were not successful—in all cases no traces of the expected 1,4-alkadienyl sulfoxides were detected. Instead complex mixtures of polymerized and decomposed products were obtained.

In conclusion, we note the following points from this investigation: (1) the 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide is readily available by reaction of phenylsulfenyl chloride with 3-methyl-1-petene-4-yn-3-ol followed by [2,3]-sigmatropic rearrangement; (2) electrophile-induced cyclization reactions of the 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide occur in all cases. The chlorination reaction leads directly to the formation of (*E*)-2-chloro-3-methylene-1,4-pentadienyl sulfoxide while interaction with bromine, sulfenyl, and selenenyl chlorides yields *5H*-1,2-oxathiol-2-ium salts. Reflux of the brominated cyclic sulfonium salt eliminates hydrogen bromide and transforms it into the (*E*)-2-bromo-3-methylene-1,4-pentadienyl sulfoxide; and (3) the 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide is a versatile synthone in organic synthesis for interesting highly unsaturated and heterocyclic compounds.

The use the prepared 3-methylene-1,4-pentadienyl sulfoxides for [4 + 2]-cycloadditions is the object of ongoing investigations. A continuation of these studies toward the synthesis and electrophile-induced cyclization reactions of other alkatrienyl sulfoxides and sulfones is currently in progress.

EXPERIMENTAL

Method of Analysis

NMR spectra were obtained on a BRUKER DRX-250 spectrometer for solutions in $CDCl_3$. Chemical shifts are in parts per million downfield from internal TMS (^1H and ^{13}C).

IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. All reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purify on TLC plates.

Starting Materials

Methylsulfenyl chloride was freshly prepared from dimethyl disulfide and chlorine in dichloromethane and used without purification. Phenylsulfenyl chloride was prepared from diphenyl disulfide and sulfuryl chloride in dichloromethane and distilled in vacuo (b. p. 80–81/20 mm Hg) before used. 3-Methyl-1-pentene-4-yn-3-ol and phenylselenenyl chloride were commercially available and were purified by usual methods.

Synthesis of 3-Methyl-1,2,4-pentatrienyl Phenyl Sulfoxide (3)

To a solution of the mixture of the 3-methyl-1-pentene-4-yn-3-ol (**1**) (30 mmol) and triethylamine (33 mmol) in dry diethyl ether (100 ml) at $-40^\circ C$ was added dropwise with stirring a solution of freshly distilled phenylsulfenyl chloride (30 mmol) in the same solvent (20 ml). The reaction mixture was stirred for 1 h at the same temperature and for 3 h at room temperature. Then the mixture was washed with water, quenched with 2N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and hexane as a eluent to give the pure product as a light yellow oil, which had the following properties.

Yield 85%, yellow oil. Eluent for TLC: ethyl acetate: hexane 2:1, R_f 0.53. Anal. Calcd. for $C_{12}H_{12}OS$ (MW 204.282), %: S 16.02. Found, %:

S 15.70. ^{1}H NMR spectrum, δ: 1.98 (s, 3H, Me), 4.86–5.17 (m, 2H, =CH_2), 6.05 (s, 1H, =C^{1}H), 6.14–6.22 (m, 1H, =C^{4}H), 7.44–8.06 (m, 5H, Ph). ^{13}C NMR spectrum, δ: 18.87, 89.79, 119.37, 113.33, 120.11, 124.72, 126.97, 130.54, 148.91, 196.52. IR spectrum (neat), cm^{-1}: 1074 (S=O), 1438, 1481 (Ph), 1614 (C=C), 1948 (C=C=C).

Electrophile-Induced Cyclic Reactions of the 3-Methyl-1,2,4-pentatrienyl Phenyl Sulfoxide (3)

General Procedure

To a solution of the 3-methyl-1,2,4-pentatrienyl phenyl sulfoxide (**3**) (10 mmol) in dry dichloromethane (20 ml) at −10°C was added dropwise with stirring a solution of the electrophilic reagent (sulfuryl chloride, bromine, methyl- or phenylsulfenyl chloride, phenylselenenyl chloride) (10 mmol) in the same solvent (10 ml). The reaction mixture was stirred for 1 h at the same temperature and for 3 or 4 h at room temperature. In the case of bromination, dry ether was added to the reaction mixture and the light brown crystals that precipitated were filtered and washed with dry ether to give the pure product. In the other cases, the solvent was removed using a rotatory evaporator and the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and hexane as a eluent to give the pure products, which had the following properties:

*(**E**)-2-chloro-3-methylene-1,4-pentadienyl phenyl sulfoxide (**4**):* Yield 62%, oil. Eluent for TLC: ethyl acetate:hexane1:25, R_f 0.47. Anal. Calcd. for $C_{12}H_{11}OSCl$ (MW 238.188), %: S 13.46, Cl 14.886. Found, %: S 13.36, Cl 14.98. ^{1}H NMR spectrum, δ: 4.58–5.02 (m, 1H, C=C$\underline{H}_aH_b$), 5.01–5.09 (m, 1H, C=C$H_a\underline{H}_b$), 5.00–5.13 (m, 1H, CH_a=C$\underline{H}_aH_b$), 5.18–5.31 (m, 1H, CH_a=$CH_a\underline{H}_b$), 6.35–6.43 (m, 1H, C$\underline{H}_a$=CH_aH_b), 6.58 (s, 1H,=CH), 7.35–8.04 (m, 5H, Ph). ^{13}C NMR spectrum, δ: 119.45, 127.21, 128.33, 129.12, 131.53, 132.75, 136.87, 143.72, 145.46, 147.45. IR spectrum (neat), cm^{-1}: 1071 (S=O), 1442, 1484 (Ph), 1596, 1612, 1621, 1668 (C=C).

*4-Bromo-5-methyl-2-phenyl-5-vinyl-5H-1,2-oxathiol-2-ium bromide (**5**):* Yield 87%, m. p. 151–152°C. Eluent for TLC: ethyl acetate:hexane 2:1, R_f 0.72. Anal. Calcd. for $C_{12}H_{12}OSBr_2$ (MW 364.09), %: S 8.81, Br 43.89. Found, %: S 9.03, Br 43.87. ^{1}H NMR spectrum, δ: 2.87 (s, 3H, Me), 5.29 (dd, $^3J_{HH}$ 9.8 Hz, $^2J_{HH}$ 1.3 Hz, 1H, CH_a=C$\underline{H}_aH_b$), 5.47 (dd, $^3J_{HH}$ 17.8 Hz, $^2J_{HH}$ 1.3 Hz, 1H, CH_a=$CH_a\underline{H}_b$), 5.92–6.03 (m, C$\underline{H}_a$=CH_aH_b), 7.21 (s, 1H,=CH), 7.28–7.79 (m, 5H, Ph). ^{13}C NMR spectrum, δ: 26.42, 85.93, 112.02, 118.47, 124.31, 126.55, 131.26, 135.44, 136.77, 142.87. IR spectrum (nujol), cm^{-1}: 1439, 1476 (Ph), 1574, 1617 (C=C).

A solution of the 4-bromo-5-methyl-2-phenyl-5-vinyl-5*H*-1,2-oxathiol-2-ium bromide (**5**) (5 mmol) in dry 1,2-dichloroethane (10 ml) was heated at reflux for 1.5 h, after which the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and hexane as an eluent to give the pure product, which had the following properties.

*(E)-2-bromo-3-methylene-1,4-pentadienyl phenyl sulfoxide (**6**):* Yield 61%, oil. Eluent for TLC: ethyl acetate:hexane1:10, R_f 0.54. Anal. Calcd. for $C_{12}H_{11}OSBr$ (MW 283.18), %: S 11.32, Br 28.22. Found, %: S 11.16, Br 28.39. ^{1}H NMR spectrum, δ: 4.65–5.05 (m, 1H, C=C$\underline{H}_a$H$_b$), 4.91–5.11 (m, 1H, C=CH$_a\underline{H}_b$), 5.06–5.19 (m, 1H, CH$_a$=C$\underline{H}_a$H$_b$), 5.17–5.29 (m, 1H, CH$_a$=CH$_a\underline{H}_b$), 6.43–6.52 (m, 1H, C$\underline{H}_a$=CH$_a$H$_b$), 6.85 (s, 1H,=CH), 7.52–8.28 (m, 5H, Ph). ^{13}C NMR spectrum, δ: 118.14, 125.22, 126.03, 129.93, 130.22, 130.88, 145.34, 147.11, 148.52, 148.96. IR spectrum (neat), cm^{-1}: 1076 (S=O), 1448, 1487 (Ph), 1601, 1611, 1624, 1655 (C=C).

*5-methyl-2-phenyl-4-methylthio-5-vinyl-5H-1,2-oxathiol-2-ium chloride (**7**):* Yield 74%, yellow oil. Eluent for TLC: ethyl acetate:hexane 2:1, R_f 0.82. Anal. Calcd. for $C_{12}H_{12}OS_2Cl$ (MW 286.839), %: S 22.36, Cl 12.36. Found, %: S 22.92, Cl 12.16. ^{1}H NMR spectrum, δ: 2.69 (s, 3H, MeS), 2.87 (s, 3H, Me), 5.09 (dd, $^3J_{HH}$ 10.2 Hz, $^2J_{HH}$ 1.2 Hz, 1H, CH$_a$=C$\underline{H}_a$H$_b$), 5.43 (dd, $^3J_{HH}$ 18.1 Hz, $^2J_{HH}$ 1.2 Hz, 1H, CH$_a$=CH$_a\underline{H}_b$), 6.14–6.28 (m, 1H, C$\underline{H}_a$=CH$_a$H$_b$), 6.86 (s, 1H,=CH), 6.73–8.11 (m, 5H, Ph). ^{13}C NMR spectrum, δ: 15.34, 25.32, 88.43, 95.78, 112.91, 128.55, 129.15, 130.76, 135.54, 144.03, 162.33. IR spectrum (neat), cm^{-1}: 1440, 1484 (Ph), 1580, 1626 (C=C).

*5-methyl-2-phenyl-4-phenylthio-5-vinyl-5H-1,2-oxathiol-2-ium chloride (**8**):* Yield 69%, yellow oil. Eluent for TLC: ethyl acetate:hexane 2:1, R_f 0.71. Anal. Calcd. for $C_{18}H_{17}OS_2Cl$ (MW 348.905), %: S 18.38, Cl 10.16. Found, %: S 18.76, Cl 10.32. ^{1}H NMR spectrum, δ: 2.77 (s, 3H, Me), 5.43 (dd, $^3J_{HH}$ 10.2 Hz, $^2J_{HH}$ 1.2 Hz, 1H, CH$_a$=C$\underline{H}_a$H$_b$), 5.39 (dd, $^3J_{HH}$ 18.1 Hz, $^2J_{HH}$ 1.2 Hz, 1H, CH$_a$=CH$_a\underline{H}_b$), 6.54–6.78 (m, 1H, C$\underline{H}_a$=CH$_a$H$_b$), 6.90 (s, 1H,=CH), 6.82–8.09 (m, 10H, 2Ph). ^{13}C NMR spectrum, δ: 29.34, 87.22, 112.32, 117.65, 123.95, 125.92, 126.65, 127.44, 127.86, 129.92, 135.04, 137.24, 147.66, 159.77. IR spectrum (neat), cm^{-1}: 1443, 1472 (Ph), 1577, 1620 (C=C).

*5-methyl-2-phenyl-4-phenylseleno-5-vinyl-5H-1,2-oxathiol-2-ium chloride (**9**):* Yield 62%, yellow oil. Eluent for TLC: ethyl acetate:hexane 3:1, R_f 0.53. Anal. Calcd. for $C_{18}H_{17}OSClSe$ (MW 395.815), %: S 8.10, Cl 8.956. Found, %: S 8.02, Cl 9.12. ^{1}H NMR spectrum, δ: 2.84 (s, 3H, Me), 5.14 (dd, $^3J_{HH}$ 10.0 Hz, $^2J_{HH}$ 1.2 Hz, 1H, CH$_a$=C$\underline{H}_a$H$_b$), 5.26 (dd, $^3J_{HH}$ 18.2 Hz, $^2J_{HH}$ 1.2 Hz, 1H, CH$_a$=CH$_a\underline{H}_b$), 6.74–7.11

(m, 1H, C$\underline{H}_a$=C$H_a H_b$), 6.95 (s, 1H, =CH), 7.51–8.22 (m, 10H, 2Ph). ^{13}C NMR spectrum, δ: 23.7, 89.04, 108.45, 117.74, 124.29, 127.55, 129.03, 130.07, 131.14, 133.44, 134.87, 135.2, 144.82, 156.64. IR spectrum (neat), cm^{-1}: 1448, 1475 (Ph), 1583, 1622 (C=C).

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