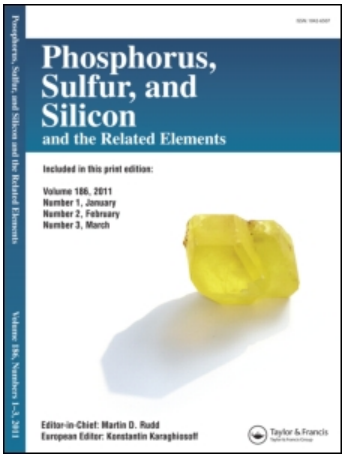

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ALKATRIENYL SULFOXIDES AND SULFONES. PART IV. SYNTHESIS AND ELECTROPHILE-INDUCED CYCLIZATION REACTIONS OF 3-METHYL-1-METHYLSULFONYLPENTA-1,2,4-TRIENE

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*A method for synthesis of 3-methyl-1-methylsulfonylpenta-1,2,4-triene (**3**) by [2,3] sigmatropic rearrangement of 3-methylpent-1-en-4-yn-3-yl methanesulfinate (**2**), formed in the reaction of 3-methylpent-1-en-4-yn-3-ol (**1**) with methylsulfinyl chloride has been found. Electrophile-induced reactions of the vinylallenyl sulfone (**3**) occur in different pathways depending on the used electrophiles. The halogenation leads to the formation of (1E)-2-halo-3-methylene-1-methylsulfonylpenta-1,4-dienes (**4**) and (**5**). Reactions with phenylsulfenyl and phenylselenenyl chlorides afford only heterocyclic products, 3-methyl-2-[methylsulfonylmethyl]thiophene (**6**) in the case of sulfenyl chloride, and a mixture of 2,5-dihydroselenophene (**7**) and selenophene (**8**) in the case of selenenyl chloride.*

Keywords: 2,5-Dihydro-selenophene; electrophile-induced cyclization reactions; selenophene; thiophene; vinylallenyl sulfone

INTRODUCTION

In the past three decades, synthesis and use of allene derivatives have been expanded in preparative organic chemistry. An impressive

Dedicated to Professor Dr. Marko Kirilov, Dr. Sc., from University of Sofia, Sofia, Bulgaria, on the occasion of his 80th birthday, and Professor Dr. Christo M. Angelov, Dr. Sc., from University of Alberta, Edmonton, Canada, on the occasion of his 60th birthday.

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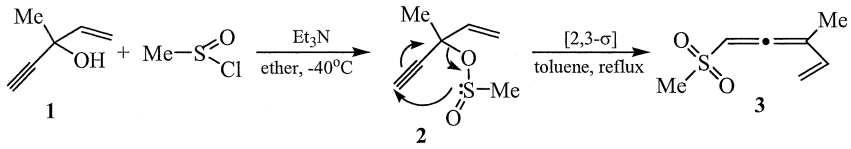
number of heterocyclic systems has been prepared from allenic starting materials. One of the characteristic reactions of the allenes is the electrophilic addition reaction, in which the addition products of the reagent to the one and/or other double bond of the allenic system are usually obtained.[2] Functionalized allenes are very interesting substrates as a material of choice to study the electrophilic addition reactions on the carbon–carbon double bonds.[2d,2e] 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[2d,2e] 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) show that various five-membered heterocyclizations proceed in most cases.[3b,3d,4] 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,[5] while the interaction with sulfenyl[5d,6] and selenenyl[5c,5d,7] chlorides gives the thiophene- or selenophene-2- or 3-phosphonates.

There are methods[3] for the synthesis of sulfur-containing allenes (sulfoxides,[3a–3c] sulfinates,[3d] sulfinamides,[3e,3f] and sulfones[3g,3h]), 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 Okamura and coworkers in a variety of preparations and interesting reactions of allenyl sulfoxides,[8a–8d] including the preparation of vinylallenes,[8] which are useful intermediates in organic synthesis in general[8e] and natural polyenes, such as vitamins A and D, in particular.[8f]

As part of our program[1] on the synthesis and cyclization reactions of alkatrienyl sulfoxides and sulfones, we now report the results on the synthesis of 3-methyl-1-methylsulfonylpenta-1,2,4-triene and the reactions with some electrophilic reagents (sulfuryl chloride, bromine, phenylsulfenyl chloride, and phenylselenenyl chloride) for study of the electrophile-promoted cyclization reactions.

RESULTS AND DISCUSSION

Since its discovery three decades ago,[3g,3h] the reversible interconversion of propargylic sulfinates to allenyl sulfones 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 total synthesis of a variety of natural products such as steroids, prostaglandins, and leukotrienes.[4a] Our strategy for the synthesis of 3-methyl-1-methylsulfonylpenta-1,2,4-triene (**3**), using our experience on the preparation of the 1,2,4-pentatrienyl sulfoxide[1a] and 1,3,4-hexatrien-3-yl sulfoxide[1b] and sulfone[1c] relies on the well-precedented [2,3] sigmatropic shift of propargylic sulfinates to α-allenic sulfones.[3g,3h] This compound was prepared in 31% overall yield by reaction of freshly distilled methylsulfinyl chloride with 3-methylpent-1-en-4-yn-3-ol (**1**) in the presence of triethylamine and following [2,3] sigmatropic rearrangement of the formed 3-methylpent-1-en-4-yn-3-yl methanesulfinate (**2**) in toluene at reflux according to Scheme 1. After a conventional workup, the resulting compound (**3**) was isolated by column chromatography as a light yellow oil and identified by ^{1}H and ^{13}C NMR and infrared (IR) spectra as well as elemental analysis.

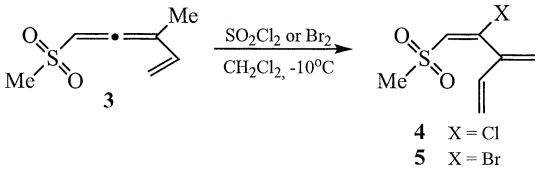


SCHEME 1

The alkatrienyl sulfone (**3**) 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 to sulfur-containing allenes,[3b,3d,4] to phosphorylated alkatrienes,[5–7] and to 1,2,4-pentatrienyl[1a] and 1,3,4-hexatriene-3-yl sulfoxides[1b] and sulfone,[1c] the following pathways of the reactions could be assumed: (1) attack of the reagent on the C^2—C^3 double bond with formation of 2,3-adduct, (2) 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, (3) 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 (sulfone group) and ring closure to five-membered cyclic compound, (4) attack

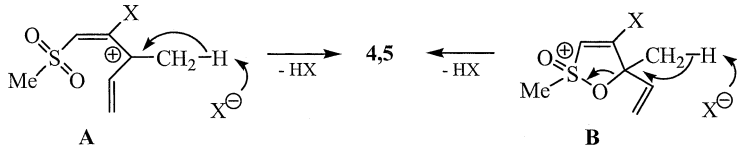
of the reagent on the C^2—C^3 double bond of the trienic system and following neighboring group participation of the C^4—C^5 double bond and ring closure to cyclic compound, (5) attack of the reagent on the C^1—C^2 double bond with formation of 1,2-adduct, and (6) elimination reactions after realization of some of above-mentioned pathways (1 to 5).

We established that reactions of the trienyl sulfone (**3**) with sulfuryl chloride or bromine in dichloromethane proceeded with formation of (1*E*)-2-halo-3-methylene-1-methylsulfonylpenta-1,4-dienes (**4**) and (**5**) in 88% yield, according to the reaction sequence outlined in Scheme 2.



SCHEME 2

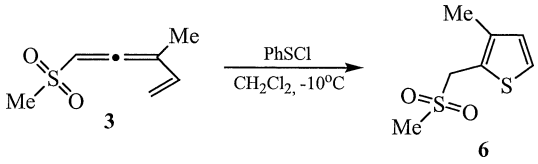
The resulting compounds (**4**) and (**5**) were isolated by column chromatography as crystals and identified by ^1H and ^{13}C NMR and IR spectra as well as elemental analysis. Mechanistic rationale for the formation of the 1,3,5-trienyl sulfones (**4**) and (**5**) in elimination reaction of hydrogen 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 carbenium ion (**A**) and following elimination of hydrogen halide after an attack of halide anion on one hydrogen of the methyl groups, as has been shown by Braverman and Reisman[9] in the case of halogenation of allenyl sulfones; and (2) deprotonation in the stage of the in situ generated cyclic sulfonium halide (**B**) as shown by Horner and Binder[7] in the reaction of allenyl sulfoxides with electrophilic reagents. The results reported before[1a] confirm our second assumption that the reaction of vinylallenyl sulfone (**3**) with halogens leading to the preparation of the 3-halohexatrienes (**4**) and (**5**) probably proceed through the cyclic sulfonium halide (**B**). Moreover, the configuration of the sulfones (**4**) and



SCHEME 3

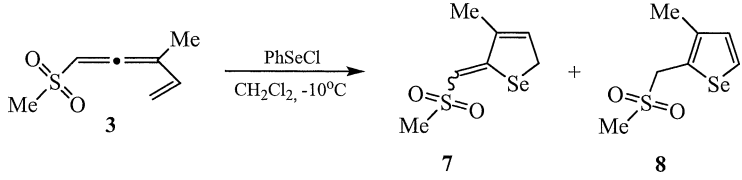
(**5**), assigned on the base of the chemical shift value[12] of the olefinic proton at C^1 atom, is most likely to be (*E*). In addition, the intermediate formation of the cyclic sulfonium salts (**B**) predetermines the (*E*) configuration of the 2-halo-1-methylsulfonylpenta-1,4-dienes (**4**) and (**5**).

Reaction of the vinylallenyl sulfone (**3**) with phenylsulfenyl chloride was carried out with electrophile-promoted cyclization by neighboring participation of the C^4—C^5 double bond and ring closure to give 3-methyl-2-[methylsulfonylmethyl]thiophene (**6**) in 71% yield, as shown in Scheme 4:



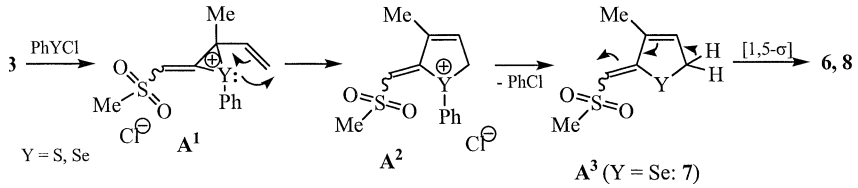
SCHEME 4

In a similar way, a *ca.* 1:1 mixture of 3-methyl-2-[methylsulfonylmethylene]-2,5-dihydroselenophene (**7**) and 3-methyl-2-[methylsulfonylmethyl]selenophene (**8**) was obtained with 65% overall yield from the reaction of the vinylallenyl sulfone (**3**) with phenylselenenyl chloride in dry dichloromethane at -10°C, according to the reaction sequence outlined in Scheme 5. Resulting dihydroselenophene (**7**) and selenophene (**8**) were isolated by column chromatography and identified by ^{1}H and ^{13}C NMR and IR spectra as well as elemental analysis. The obtained compounds (**7**) and (**8**) 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.[9]



SCHEME 5

The chemical transformations thus observed (Schemes 4 and 5) are in accordance with the following reaction mechanisms (see Scheme 6). The initial act is the attack of electrophilic sulfur or selenium on the



SCHEME 6

most nucleophilic atom of the trienic system of π-bonds (C^2) with the formation of the cyclic onium (thiiranium or seleniranium) ions ($\mathbf{A}^1$) after an attack on the C^2—C^3 double bond. The ions ($\mathbf{A}^1$) are in the plane of the π-bond of the vinyl group (*s-cis* conformation), and for this reason ($\mathbf{A}^1$) are easily transformed into the more stable five-membered cyclic ions ($\mathbf{A}^2$). Furthermore, the ions ($\mathbf{A}^2$) are transmuted into the intermediate ($\mathbf{A}^3$) by elimination of chlorobenzene, which was isolated and identified. In the case of selenenyl chloride, the 2,5-dihydroselenophene (**7**) was isolated as yellow oil in 29% yield. A [1,5] prototropic shift and aromatization of the formed dihydrothiophene ($\mathbf{A}^3$) (not isolated) or dihydroselenophene (**7**) occurred to give the thiophene (**6**) or the selenophene (**8**). The realization of the heterocyclization process is connected with introduction of the 1,3-dienic parts of the 1,2,4-trienic system into the reaction course. This fact is obviously due to the ability of the sulfur and selenium atoms to form cyclic ions,[10] which are further transformed into five-membered heterocyclic compounds.

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

1. The 3-methyl-1-methylsulfonyl-penta-1,2,4-triene (**3**) is readily available by reaction of methylsulfinyl chloride with 3-methyl-1-pentene-4-yn-3-ol followed by [2,3] sigmatropic shift.
2. Electrophile-induced reactions of the 1,2,4-trienyl sulfone (**3**) occur in different pathways depending on the kind of electrophile. The halogenation reaction leads to formation of the highly unsaturated (1*E*)-2-halo-3-methylene-1-methylsulfonylpenta-1,4-dienes (**4**) and (**5**), while interaction with sulfenyl and selenenyl chlorides yields only heterocyclic products—the thiophene (**6**) in the case of sulfenyl chloride and a mixture of the 2,5-dihydroselenophene (**7**) and the selenophene (**8**) in the case of selenenyl chloride.
3. The 3-methyl-1-methylsulfonylpenta-1,2,4-triene (**3**) is a versatile synthon for heterocyclic 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 towards the synthesis and electrophile-induced cyclization reactions of other alkatrienyl sulfones is currently in progress.

EXPERIMENTAL

Method of Analysis

^{1}H and ^{13}C 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.

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.

Mps (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

Methylsulfinyl chloride was prepared from dimethyl disulfide and sulfuryl chloride in acetic acid and distilled in vacuo (bp 36°C/20 mm Hg) before used.[11] Phenylsulfenyl chloride was prepared from diphenyl disulfide and sulfuryl chloride in dichloromethane and distilled in vacuo (b.p., 80–81°C/20 mm Hg) before used.[13] 3-Methylpent-1-en-4-yn-3-ol and phenylselenenyl chloride were commercially available and were purified by usual methods.

Synthesis of 3-Methylpent-1-en-4-yn-3-yl Methanesulfinate (2)

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 ether (100 ml) at −40°C was added dropwise with stirring a solution of freshly distilled methylsulfinyl chloride (2.96 g, 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 rt and then washed with water, 2N HCl, extracted with ether. 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 with ethyl acetate/heptane (115:50 v/v) as eluent.

Yield 3.75 g (79%), yellow oil. Anal. Calcd for $C_7H_{10}O_2S$: C, 53.13; H, 6.37; S, 20.27. Found: C, 53.23; H, 6.34; S, 20.37. ^{1}H NMR ($CDCl_3$), δ: 1.71 (s, 3H, Me), 2.41 (s, 1H, HC≡), 3.06 (s, 3H, SO_2Me), 4.88 (dd, J_{cis} 10.8 Hz, J_{gem} 1.3 Hz, 1H, CH_a=C$\underline{H}_a$H$_b$), 5.73 (dd, J_{trans} 17.3 Hz, J_{gem} 1.3 Hz, 1H, CH_a=$CH_a\underline{H}_b$), 6.22 (dd, J_{cis} 10.8 Hz, J_{trans} 17.3 Hz, 1H, C$\underline{H}_a$=CH_aH_b). ^{13}C NMR ($CDCl_3$), δ: 26.4, 46.8, 64.4, 72.1, 84.3, 120.7, 140.6. IR (neat), cm^{-1}: 1128 (S=O), 1611 (C=C), 2096 (C≡C), 3284 (HC≡).

Synthesis of 3-Methyl-1-methylsulfonylpenta-1,2,4-triene (3)

A solution of sulfinate (**2**) (3.75 g, 23.7 mmol) in dried toluene (30 ml) was refluxed for 5 h. After evaporation of the solvent, the residue was chromatographied on a column (silica gel, ethyl acetate-heptane (124:65 v/v)) to give the pure product as light yellow oil.

Yield 39%. Anal. Calcd for $C_7H_{10}O_2S$: C, 53.13; H, 6.37; S, 20.27. Found: C, 53.22; H, 6.42; S, 20.13. ^{1}H NMR ($CDCl_3$), δ: 1.74 (s, 3H, Me), 2.96 (s, 3H, SO_2Me), 4.90 (dd, J_{cis} 10.6 Hz, J_{gem} 1.3 Hz, 1H, CH_a=C$\underline{H}_a$H$_b$), 4.97 (dd, J_{trans} 17.2 Hz, J_{gem} 1.3 Hz, 1H, CH_a=$CH_a\underline{H}_b$), 6.11 (s, 1H, =C^1–H), 6.27 (dd, J_{cis} 10.6 Hz, J_{trans} 17.2 Hz, 1H, C$\underline{H}_a$=CH_aH_b). ^{13}C NMR ($CDCl_3$), δ: 17.8, 43.7, 98.4, 104.15, 119.5, 128.3, 206.7. IR (neat), cm^{-1}: 1118, 1299 (SO_2), 1609 (C=C), 1954 (C=C=C).

Electrophile-Induced Reactions of the 3-Methyl-1-methylsulfonylpenta-1,2,4-triene (3)

General Procedure

To a solution of triene (**3**) (1.58 g, 10 mmol) in dry dichloromethane (20 ml) at −10°C was added dropwise with stirring a solution of electrophilic reagent (sulfuryl chloride, bromine, 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 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 (200:90 v/v) as eluent. The pure products had the properties detailed below.

(1E)-2-Chloro-3-methylene-1-methylsulfonylpenta-1,4-diene ***(4)***. Yield 88%, pale yellow crystals, m.p. 88–89°C (from benzene/ethyl acetate 2:1). Anal. Calcd for $C_7H_9O_2ClS$: C, 43.63; H, 4.71; S, 16.64, Cl, 18.40. Found: C, 43.69; H, 4.82; S, 16.43; Cl, 18.64. ^{1}H NMR ($CDCl_3$),

δ: 2.87 (s, 3H, SO_2Me), 4.44 (m, J 0.7 Hz, J_{gem}1.6 Hz, 1H, C=$CH_a\underline{H}_b$), 5.08 (m, J1.1 Hz, J_{gem} 1.6 Hz, 1H, C=$C\underline{H}_aH_b$), 5.19 (m, J_{gem}1.3 Hz, J_{cis} 9.7 Hz, 1H, CH=$C\underline{H}_aH_b$), 5.24 (m, J_{gem} 1.3 Hz, J_{trans} 16.8 Hz, 1H, CH=$CH_a\underline{H}_b$), 6.67 (m, J_{cis} 9.7 Hz, J_{trans} 16.8 Hz, 1H, $C\underline{H}$=CH_aH_b), 6.81 (m, J 0.7 Hz, J 1.1 Hz, 1H, =C^1–H). ^{13}C NMR ($CDCl_3$), δ: 43.5, 123.65, 132.4, 135.7, 141.45, 143.3, 146.6. IR (nujol), cm^{-1}: 1121, 1296 (SO_2), 1600–1628 (C=C).

*(1E)-2-Bromo-3-methylene-1-methylsulfonylpenta-1,4-diene (**5**).* Yield 88%, pale brown crystals, m.p. 81–82°C (from benzene/ethyl acetate 2:1). Anal. Calcd for $C_7H_9O_2BrS$: C, 35.45; H, 3.83; S, 13.52; Br, 33.67. Found; C, 35.41; H, 3.87; S, 13.43; Br, 33.81. ^{1}H NMR ($CDCl_3$), δ: 3.02 (s, 3H, SO_2Me), 4.80 (m, J 0.7 Hz, J_{gem} 1.7 Hz, 1H, C=$CH_a\underline{H}_b$), 4.99 (m, J_{gem} 1.3 Hz, J_{cis} 9.9 Hz, 1H, CH=$C\underline{H}_aH_b$), 5.05 (m, J1.1 Hz, J_{gem} 1.7 Hz, 1H, C=$C\underline{H}_aH_b$), 5.12 (m, J_{gem} 1.3 Hz, J_{trans} 16.5 Hz, 1H, CH=$CH_a\underline{H}_b$), 6.58 (m, J_{cis} 9.9 Hz, J_{trans} 16.5 Hz, 1H, $C\underline{H}$=CH_aH_b), 7.32 (m, J 0.7 Hz, J 1.1 Hz, 1H, =C^1–H). ^{13}C NMR ($CDCl_3$), δ: 43.5, 122.15, 131.1, 136.1, 149.25, 149.8, 150.9. IR (nujol), cm^{-1}: 1124, 1300 (SO_2), 1597–1622 (C=C).

*3-Methyl-2-[methylsulfonylmethyl]thiophene (**6**).* Yield 71%, pale yellow crystals, m.p. 75–76°C (from hexane/ethyl acetate 3:1). Anal. Calcd for $C_7H_{10}O_2S_2$: C, 44,18; H, 5.30; S, 33.70. Found: C, 44.30; H, 5.26; S, 33.48. ^{1}H NMR ($CDCl_3$), δ: 2.10 (s, 3H, Me), 3.07 (s, 3H, SO_2Me), 4.31 (s, 2H, CH_2), 6.41 (d, J 5.3 Hz, 1H, βH), 6.95 (d, J 5.3 Hz, 1H, αH). ^{13}C NMR ($CDCl_3$), δ: 14.5, 43.1, 59.95, 130.25, 131.2, 132.1, 143.4. IR (nujol), cm^{-1}: 1127, 1300 (SO_2), 1468, 1556 (thiophene).

*3-Methyl-2-[methylsulfonylmethylene]-2,5-dihydroselenophene (**7**).* Yield 29%, yellow oil. Anal. Calcd for $C_7H_{10}O_2SeS$: C, 35.45; H, 4.25; S, 13.52. Found: C, 35.50; H, 4.23; S, 13.69. ^{1}H NMR ($CDCl_3$), δ: 1.98 (s, 3H, Me), 2.79 (s, 3H, SO_2Me), 3.71, 3.80 (dd, J 2.0 Hz, J 20.2 Hz, 2H, CH_2), 5.84 (t, J 2.0 Hz, 1H, =C^4–H), 7.30 (*Z*), 6.94 (*E*) (*Z*:*E* = 3:1) (ss, 1H, =C–H). ^{13}C NMR ($CDCl_3$), δ: 23.1, 24.9 (J 38.2 Hz), 38.7, 119.5, 127.4 (*Z*), 125.2 (*E*) (*Z*:*E* = 3:1), 142.6 (*Z*), 140.1 (*E*) (*Z*:*E* = 3:1) (J 68.5 Hz), 149.4. IR (nujol), cm^{-1}: 1124, 1294 (SO_2), 1468, 1578, 1599 (C=C).

*3-Methyl-2-[methylsulfonylmethyl]selenophene (**8**).* Yield 36%, yellow oil. Anal. Calcd for $C_7H_{10}O_2SeS$: C, 35.45; H, 4.25; S, 13.52. Found: C, 35.52; H, 4.31; S, 13.38. ^{1}H NMR ($CDCl_3$), δ: 2.46 (s, 3H, Me), 2.88 (s, 3H, SO_2Me), 4.08 (s, 2H, CH_2), 6.19 (dd, J 4.8 Hz, J 9.7 Hz, 1H, βH), 7.38 (dd, J 4.8 Hz, J 46.7 Hz, 1H, αH). ^{13}C NMR ($CDCl_3$), δ: 18.4, 38.2, 59.7, 120.15 (J 66.1 Hz), 132.8, 138.9 (J 53.8 Hz), 143.2. IR (nujol), cm^{-1}: 1119, 1291 (SO_2).

REFERENCES

[1] a) V. Ch. Christov and I. K. Ivanov, *Phosphorus, Sulfur and Silicon*, **177,** 2445 (2002); b) V. Ch. Christov and I. K. Ivanov, *Sulfur Lett.*, **25,** 191 (2002); c) V. Ch. Christov and I. K. Ivanov, *Heterocyclic Commun.*, **9,** 629 (2003).

[2] a) M. C. Caserio, In *Selective Organic Transformations*, edited 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) G. H. Schmid and D. G. Garratt, In *The Chemistry of Double-bonded Functional Groups*, edited by S. Patai (Wiley-Interscience, New York, 1977), Chap. 9, pp. 725–912; d) T. L. Jacobs, In *The Chemistry of the Allenes*, edited by S. R. Landor (Academic Press, New York, 1982), Vol. 2, Chap. 4, pp. 417–510; e) W. Smadja, *Chem. Rev.*, **83,** 263 (1983).

[3] a) S. Braverman and Y. Stabinsky, *Isr. J. Chem.*, **5,** 125 (1967); b) L. Horner and V. Binder, *Liebigs Ann. Chem.*, **757,** 33 (1972); c) A. Padwa, W. H. Bullock, B. H. Norman, and J. Perumattam, *J. Org. Chem.*, **56,** 4252 (1991); d) S. Braverman and D. Reisman, *Tetrahedron Lett.*, **18,** 1753 (1977); e) J.-B. Baudin, S. Julia, and Y. Wang, *Tetrahedron Lett.*, **30,** 4965 (1989); f) J.-B. Baudin, I. Bkouche-Waksman, S. Julia, C. Pascard, and Y. Wang, *Tetrahedron*, **47,** 3353 (1991); g) G. Smith and C. J. M. Stirling, *J. Chem. Soc.* (C), 1530 (1971); h) S. E. Denmark, M. A. Harmata, and K. S. White, *J. Org. Chem.*, **52,** 4031 (1987).

[4] a) S. Braverman, In *The Chemistry of Sulphones and Sulphoxides*, edited by S. Patai, Z. Rappoport, and C. J. M. Stirling (John Wiley & Sons, New York, 1988), pp. 717–757; b) S. Braverman and D. Reisman, *J. Am. Chem. Soc.*, **99,** 605 (1977); c) S. Braverman, *The Chemistry of Sulphinic Acids, Esters and their Derivatives*, edited by S. Patai (John Wiley & Sons, New York, 1990), pp. 297–349.

[5] a) Ch. M. Angelov, M. Kirilov, B. I. Ionin, and A. A. Petrov, *Zh. Obshch. Khim.*, **49,** 2225 (1979); b) Ch. M. Angelov, N. M. Stojanov, and B. I. Ionin, *Zh. Obshch. Khim.*, **52,** 178 (1982); c) Ch. M. Angelov and Ch. Z. Christov, *Synthesis*, 664 (1984); d) Ch. M. Angelov, D. D. Enchev, and M. Kirilov, *Phosphorus and Sulfur*, **35,** 35 (1988).

[6] a) Ch. M. Angelov, M. Kirilov, K. V. Vachkov, and S. L. Spassov, *Tetrahedron Lett.*, **21,** 3507 (1980); b) Ch. M. Angelov and K. V. Vachkov, *Tetrahedron Lett.*, **22,** 2517 (1981).

[7] a) Ch. M. Angelov and Ch. Z. Christov, *Phosphorus and Sulfur*, **15,** 373 (1983); b) T. N. Tancheva, Ch. M. Angelov, and D. M. Mondeshka, *Heterocycles*, **23,** 843 (1985).

[8] a) E. M. G. A. van Kruchten and W. H. Okamura, *Tetrahedron Lett.*, **23,** 1019 (1982); b) W. Reischl and W. H. Okamura, *J. Am. Chem. Soc.*, **104,** 6115 (1982); c) W. H. Okamura, R. Peter, and W. Reischl, *J. Am. Chem. Soc.*, **107,** 1034 (1985); d) W. H. Okamura, G.-Y. Shen, and R. Tapia, *J. Am. Chem. Soc.*, **108,** 5018 (1986); e) I. Z. Egenburg, *Russ. Chem. Rev.*, **47,** 900 (1978); f) W. H. Okamura, *Acc. Chem. Res.*, **16,** 81 (1983).

[9] M. P. Simonin, M. J. Pauet, J. M. Gense, and C. Paumier, *Org. Magn. Resonance*, **8,** 508 (1976).

[10] a) G. Capozzi, G. Modena, and L. Pasquato, In *The Chemistry of Sulphenyl Halides and Sulphenamides*, edited by S. Patai (John Wiley & Sons, Chichester, 1990), Chap. 10; b) G. H. Schmid and D. G. Garratt, *Tetrahedron Lett.*, **16,** 3991 (1975).

[11] J.-H. Youn and R. Herrman, *Tetrahedron Lett.*, **27,** 1493 (1986).

[12] E. Pretsch, J. Seibl, W. Simon, and T. Clerc, *Tabellen zur Structuraufklärung organischer Verbindungen mit spectrockopischen Methoden* (Springer-Verlag, Berlin, Heidelberg, New York, 1981), p. 149.

[13] H. Lecher and F. Holschneider, *Ber.*, **57,** 755 (1924).