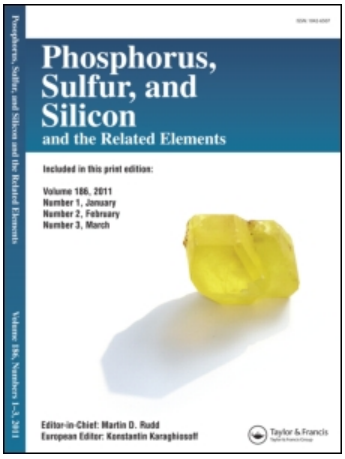


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

S-CONTAINING PROPARGYL COMPOUNDS: SYNTHESIS AND IR STUDY[1]

Valerij Ch. Christov[a]; Jordanka I. Tacheva[a]; Veselin T. Vasilev[a]; Christo M. Angelov[a]
[a] Department of Chemistry, University of Shoumen, Shoumen, Bulgaria

To cite this Article Christov, Valerij Ch. , Tacheva, Jordanka I. , Vasilev, Veselin T. and Angelov, Christo M.(1993) '*S*-CONTAINING PROPARGYL COMPOUNDS: SYNTHESIS AND IR STUDY[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 78: 1, 199 — 206
To link to this Article: DOI: 10.1080/10426509308032435
URL: http://dx.doi.org/10.1080/10426509308032435

Phosphorus, Sulfur, and Silicon, 1993, Vol. 78, pp. 199–206
Reprints available directly from the publisher
Photocopying permitted by license only

S-CONTAINING PROPARGYL COMPOUNDS: SYNTHESIS AND IR STUDY[1]

VALERIJ CH. CHRISTOV,† JORDANKA I. TACHEVA,
VESELIN T. VASILEV and CHRISTO M. ANGELOV
Department of Chemistry, University of Shoumen, 9700 Shoumen, Bulgaria

(Received August 13, 1992; in final form October 21, 1992)

N-Propargylsulfeneamides 2–5 and *N*-propargylmethanesulfineamides 6 and 7 have been synthesized from *N*-propargylamines 1 and sulfenyl halides or methylsulfinyl chloride, respectively. In a similar way, propargylmethanesulfinates 8 and 9 have been obtained from the corresponding propargyl alcohols and methylsulfinyl chloride. The IR spectral study on the existence of intermolecular and/or intramolecular hydrogen bonds in *S*-containing propargyl compounds 6–9 has been carried out.

Key words: *N*-propargylsulfeneamides; *N*-propargylmethanesulfineamides; propargylmethanesulfinates; IR spectral study; intermolecular and intramolecular hydrogen bonds.

INTRODUCTION

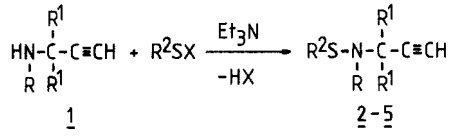
The interaction of propargyl alcohols with halogen-containing reagents as sulfenyl halides[3] and sulfinyl chlorides[4] is a convenient method for obtaining propargyl compounds (sulfenates or sulfinates) which usually undergo [2,3]-sigmatropic rearrangement to allenic products[3–6] (sulfoxides or sulfones). On the other hand there are some publications[7] concerning the synthesis of phosphorylated *N*-propargylamines. It seems that the above mentioned rearrangement is not typical for the phosphorylated *N*-propargylamines. There is only one communication[7a] where the acetylene-allenic isomerization of *N*-propargylaminophosphates caused by sodium hydride in tetrahydrofuran and followed by a prototropic isomerization of the obtained allenes to the corresponding acetylenic derivatives is described. Such a rearrangement has not been observed for the synthesized *N*-propargyl- aminophosphites.[7b,7d] However, *N*-propargylaminophosphines rearrange spontaneously with P—N bond cleavage to 2-3-dialkylphosphino-2-propenal imines.[7d] This rearrangement proceeds via addition of a proton and the phosphino group to the triple bond to give cyclic phosphonium intermediates followed by a base catalyzed elimination to obtain the products.[7d] Any data concerning the synthesis of *S*-containing *N*-propargylamines were not found in the literature.

In this paper we report our results on the synthesis of *S*-containing propargyl compounds, the attempts for an rearrangement or cyclization of the resulting compounds as well as a possible explanation of the results by an IR spectral study on the existence and the type of the hydrogen bonds in the *S*-containing propargyl compounds.

†Author to whom correspondence should be addressed.

RESULTS AND DISCUSSION

We established that when[2] the interaction between methyl- or phenylsulfenyl halides (chloride or bromide) and *N*-propargylamines 1 proceeded in the presence of triethylamine, *N*-propargylsulfeneamides 2–5 with good yields (64–69%) were isolated:



	R	R^1	R^2	X
2	Me	H	Me	Cl
3	Me	H	Ph	Cl
4	H	Me	Me	Br
5	H	Me	Ph	Cl

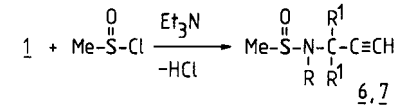
Scheme 1

The reaction was carried out in chloroform at low temperature (−30° to −25°C) and under a nitrogen atmosphere. Compounds 2–5 were isolated by vacuum distillation as light yellow liquids. The obtained sulfeneamides 2–5 were characterized by IR spectra and elemental analysis.

The attempts for [2,3]-sigmatropic rearrangement of the *N*-propargylsulfeneamides 2–5 to the corresponding allenic compounds by a prolonged staying under nitrogen at room temperature,[3b] by heating in chlorobenzene at 130°C[4a] and by treatment with NaH in tetrahydrofuran[7a] were not successful—in all cases no traces of the expected allenic compounds were detected. An explanation of this fact should be connected with the presumably less stability of the expected allenic sulfinimides[8] in comparison with the allenic sulfoxides which are obtained by a [2,3]-sigmatropic rearrangement of the oxygen analogues—the propargyl-sulfenates.[3] Also, the S=O bond (in the allenic products[9]) is stronger than the S=N bond (in the corresponding allenic products here).

The heating of the reaction mixtures of the compounds 2–5 containing as a result of their formation triethylaminehydrochloride did not lead to the corresponding *S*-containing 2-propenal imines supposedly because of the more pronounced electronegativity and the less nucleophility of the sulfur atom compared with the phosphorus in the *N*-propargylaminophosphines.[7d]

The reaction of methylsulfinyl chloride with *N*-propargylamines 1 in the presence of triethylamine in dry ether at −45°C and under a nitrogen atmosphere yielded the *N*-propargylmethanesulfineamides 6 and 7:



	R	R^1
6	Me	H
7	H	Me

Scheme 2

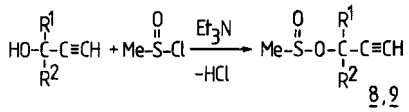
The resulting products were isolated by vacuum distillation (6) or by recrystallization from benzene (7). The structure of the new compounds 6 and 7 was determined by ^{1}H- and ^{13}C-NMR, and by IR spectroscopy.

Like the *N*-propargylsulfeneamides 2–5, the *N*-propargylmethanesulfineamides 6 and 7 underwent neither [2,3]-sigmatropic rearrangement to the corresponding allenic sulfoximides nor a rearrangement leading to 2-propenalimino-3-sulfoxides.

The efforts for heterocyclization of the *N*-propargylmethanesulfineamides 6 and 7 with the participation of the triple bond and the sulfoxide group by heating in different solvents, by treatment with triethylaminehydrochloride or with boron trifluoride ethyletherate were not effective as well.

In order to check the presence of the spatial arrangement of the triple bond and the sulfoxide group suitable for rearrangements and heterocyclization, an IR study on the existence of the intermolecular and/or intramolecular hydrogen bonds in the compounds 6 and 7 was performed.

With the same purpose, propargylmethanesulfinates 8 and 9 were obtained by the interaction of methylsulfinyl chloride and propargyl alcohols in the presence of triethylamine and under a nitrogen atmosphere and cooling to −60°C:



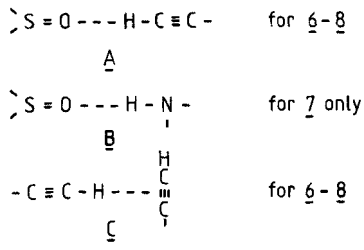
	R^1	R^2
8	Me	Me
9	Me	Et

Scheme 3

The propargyl compounds 8 and 9 underwent easily [2,3]-sigmatropic rearrangement to the corresponding allenic sulfones[4] and for this reason the IR spectra of the compounds 8 and 9 were taken immediately after their preparation, without purification by vacuum distillation.

In principle, the following types of the hydrogen bonds are possible for the compounds 6–8:

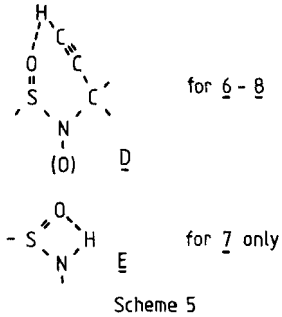
Intermolecular Hydrogen Bonds



Scheme 4

The realization of the intermolecular hydrogen bond C is practically impossible as in the molecules of 6–8 the polar oxygen or nitrogen atom is present, i.e. the association would be accomplished with these atoms rather than with the triple bond π-electrons.[10]

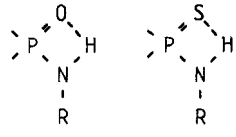
Intramolecular Hydrogen Bonds



Scheme 5

The existence of an intramolecular hydrogen bond of the type D would serve as an indication for the possibility of the heterocyclization with the participation of the sulfoxide group and the triple bond allowing the formation of the corresponding thiazolic compounds.

According to Nyqvist,[11] some phosphoric and thiophosphoric amides form intramolecular hydrogen bonds of the type E:



Scheme 6

and show several bands in the ν_{N-H} stretching vibration region. In the first case, the band for the associated N—H was observed at 3240 cm^{-1} and in the second case—at 3330 cm^{-1}. Keeping in mind the greater polarity of the S=O group

compared to P=O and especially to P=S groups, we suppose that the formation of the intramolecular hydrogen bond E for the compound 7 is possible.

In order to check which of the probable hydrogen bonds are present in the compounds under investigation, their IR spectra were recorded in the neat and in solutions of CCl_4 and $CHCl_3$ with different concentrations. The data for the characteristic frequencies of interest are summarized in the Tables I, II, and III. As

TABLE I

Characteristic frequencies of 6 (cm^{-1})

Concentration	$\nu_{\equiv C-H}$	$\nu_{S=O}$	$\delta_{\equiv CH}$
Liquid State	3270	1070	692 and 665
1.0 M	3308	1087	659 and 633
0.1 M	3308	1087	661 and 633
0.01 M	3308	1087	661 and 633
0.001 M	3308	-	-

TABLE II

Characteristic frequencies of 7 (cm^{-1})

Concentration	$\nu_{\equiv C-H}$	ν_{NH}	$\nu_{S=O}$	$\delta_{\equiv CH}$
Solid State	3217	3124	1053	657
0.1 M	3305	3155	1063	637
0.05 M	3305	3155	1063	637
0.01 M	3305	3155	-	638
0.001 M	3305	3155	-	-
0.0005 M	3305	3155	-	-

TABLE III

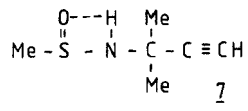
Characteristic frequencies of 8 (cm^{-1})

Concentration	$\nu_{\equiv CH}$	$\nu_{S=O}$	$\delta_{\equiv CH}$
Liquid State	3280	1125	697 and 684
1.0 M	3305	1130	667 and 638
0.1 M	3305	1130	665 and 637
0.01 M	3305	1130	665 and 637
0.001 M	3305	-	-

one could see from the Tables I and III, the transition from the liquid state to the solution leads to an increase of the stretching vibration frequencies $\nu_{\equiv CH}$ and $\nu_{S=O}$ and a decreasing of the deformation vibration frequencies $\delta_{\equiv CH}$. These frequency changes could be explained if one suggests the existence of the intermolecular hydrogen bonds of the type A which are destroyed during the dissolving process thus causing the observed shifts of the IR bands. Analogous effects were observed when the $CHCl_3$ was used as a solvent but the values of $\nu_{S=O}$ were lower probably due to the formation of hydrogen bonds with the solvent.

The transition of the compound 7 from solid state to the solution is accompanied by increasing of $\nu_{\equiv CH}$, ν_{NH} and $\nu_{S=O}$ and a decrease of $\delta_{\equiv CH}$. The dilution of the solution to 0.0005 M did not provoke other changes of the considered frequencies. Besides, while $\nu_{\equiv CH}$ was found in the expected region according to the literature data,[10] the values for the ν_{NH} were unusually low. The value of ν_{NH} did not change even at concentration of 0.0005 M (when all kinds of the intermolecular hydrogen bonds are impossible[12]).

In our opinion, the observed strong reduction of ν_{NH} is due to the formation of a stable intramolecular hydrogen bond between S=O and NH— groups (type E):



7

Scheme 7

As S=O and NH— groups of the compound 7 take part in the hydrogen bond E, an intermolecular hydrogen bond C is present in the solid state and probably is destroyed in solution causing the increase of $\nu_{\equiv CH}$ and the decrease of $\delta_{\equiv CH}$.

The absence of the intramolecular bond of the type D would be accepted as an indication for the lack of a suitable for the heterocyclization (with the participation of the triple bond and the S=O group) spatial arrangement in the molecules of the *N*-propargylmethanesulfineamides 6 and 7. Such spatial arrangement[5,6] is required to a certain extent for rearrangements which would allow the obtaining of the corresponding allene or 2-propenalimino compounds. On the other hand, the [2,3]-sigmatropic rearrangement of the propargylsulfinates to the corresponding allenic sulfones[4] in the absence of hydrogen bonds D in the compound 8 could be explained with the energetically more favourable formation of the allenic sulfones in comparison with the eventual process of the allenic sulfoximine formation from the *N*-propargylsulfineamides 6 and 7.

EXPERIMENTAL

The melting and boiling points were uncorrected. The infrared spectra were carried out on a Specord 75 IR spectrophotometer (Carl Zeiss, Jena, Germany) using the potassium bromide cells and the quartz cells for the concentration below 0.01 M.

The ^1H and ^{13}C NMR spectra in $CDCl_3$ or DMSO were recorded on a BRUKER spectrometer using TMS as the internal standard. The elemental analyses were performed at the Microanalytical unit of the University of Shoumen, Bulgaria. The methyl- and phenylsulfenyl halides were freshly prepared from the corresponding disulfides and sulfuryl chloride or bromine in chloroform and used without purification. The methylsulfinyl chloride was synthesized according to the literature.[13] All compounds were checked for their purity on TLC plates.

Preparation of the N-propargylsulfeneamides 2–5. *General procedure*: To a mixture of the *N*-methyl-*N*-propargylamine (5 mmol) or *N*-(1,1-dimethylpropargyl)amine (5 mmol) and triethylamine (5 mmol) in chloroform (30 ml), a solution of methyl- or phenylsulfenyl halides (5 mmol) in the same solvent (20 ml) is dropwise added at low temperature (−30° to −25°C) and under a nitrogen atmosphere. The reaction mixture is stirred for 2 h at the same temperature. Then the precipitate is filtered off, the solvent is removed using a rotatory evaporator, and the residue is distilled under vacuum to give the product as a light yellow liquid.

N-Methyl-N-propargylmethanesulfeneamide 2: Yield: 69%; b.p. 82–83°C/0.5 mm Hg; C_5H_9NS; Calcd., %: N 12.16, S 27.84; Found, %: N 12.31, S 28.02; IR spectra, cm^{-1}: 2138 (C≡C), 3250 (HC≡).

N-Methyl-N-propargylbenzenesulfeneamide 3: Yield: 65%; b.p. 102–103°C/0.5 mm Hg; $C_{10}N_{11}NS$; Calcd., %: N 7.90, S 18.09; Found, %: N 7.79, S 18.20; IR spectra, cm^{-1}: 2143 (C≡C), 3238 (HC≡).

N-(1,1-dimethylpropargyl)methanesulfeneamide 4: Yield: 67%; b.p. 93–94°C/0.5 mm Hg; $C_6H_{11}NS$; Calcd. %: N 10.84, S 24.81; Found, %: N 10.75, S 24.90; IR spectra, cm^{-1}: 2128 (C≡C), 3241 (HC≡).

N-(1,1-dimethylpropargyl)benzenesulfeneamide 5: Yield: 64%; b.p. 108–109°C/0.5 mm Hg; $C_{11}H_{13}NS$; Calcd., %: N 7.32, S 16.76; Found, %: N 7.54, S 16.88; IR spectra, cm^{-1}: 2131 (C≡C), 3244 (HC≡).

Preparation of the N-propargylmethanesulfineamides 6 *and* 7. *General procedure*: To a mixture of the *N*-methyl-*N*-propargylamine (5 mmol) or *N*-(1,1-dimethylpropargyl)amine (5 mmol) and triethylamine (5 mmol) in ether (30 ml), a solution of methylsulfinyl chloride (5 mmol) in the same solvent (30 ml) is dropwise added at low temperature (−40° to −45°C) and under a nitrogen atmosphere. The reaction mixture is stirred for 1 h at the same temperature and the cooling bath is removed and the mixture is stirred for 3 h at room temperature. Then the precipitate is filtered off, the solvent is removed using a rotary evaporator and the residue is distilled in the vacuum or recrystallized from benzene.

N-methyl-N-propargylmethanesulfineamide 6: Yield: 75%; b.p. 75–76°C/0.5 mm Hg; C_5H_9ONS; Calcd., %: N 10.68, S 24.43; Found, %: N 10.86, S 24.60; ^1H NMR (DMSO), ppm: 1.51 (Me—N); 2.06 (Me—S=O); 2.34 (CH_2); 3.62 (≡CH); ^{13}C NMR (DMSO), ppm: 27.72 (C—4); 46.39 (C—1); 49.41 (C—5); 75.03 (C—3); 84.95 (C—2).

N-(1,1-dimethylpropargyl)methanesulfineamide 7: Yield: 74%; m.p. 52–53°C; $C_6H_{11}ONS$; Calcd., %: N 9.65, S 22.08; Found, %: N 9.91, S 22.30; ^1H NMR ($CDCl_3$), ppm: 2.63 (Me_2C); 2.69 (Me—S=O); 3.24 (≡CH); 3.81 (NH).

Preparation of the propargylmethanesulfinates 8 *and* 9. *General procedure*: To a mixture of the 2-methyl-3-butyn-2-ol (5 mmol) and triethylamine (5 mmol) in ether (40 ml) a solution of methylsulfinyl chloride (5 mmol) in the same solvent (30 ml) is dropwise added at low temperature (−60°C) and under a nitrogen atmosphere. The reaction mixture is stirred for 1 h at the same temperature and the precipitate is filtered off. After evaporation of the solvent under reduced pressure, the crude product is used immediately for IR spectral study.

REFERENCES

1. Part of this work was presented at the 15th International Symposium on the Organic Chemistry of Sulfur, Caen, France, Poster No. PA54 (1992).
2. V. Ch. Christov, V. T. Vasilev and Ch. M. Angelov, *Sulfur Letters*, to be submitted.
3. a) S. Braverman and Y. Stabinsky, *Israel J. Chem.*, **5,** 125 (1967); *Chem. Abstr.*, **68,** 21379g (1968); b) G. Smith and C. J. M. Stirling, *J. Chem. Soc. (C)*, 1530 (1971); c) L. Horner and V. Binder, *Liebigs Ann. Chem.*, **757,** 33 (1972); d) S. Braverman and S. Sedev, *J. Am. Chem. Soc.*, **96,** 1245 (1974); e) G. Buchi and R. M. Freidinger, *J. Am. Chem. Soc.*, **96,** 3332 (1974); f) J.-B. Baudin, S. A. Julia and Y. Wang, *Tetrahedron Letters*, **30,** 4965 (1989); g) E. Block and D. Putnam, *J. Am. Chem. Soc.*, **112,** 4072 (1990); h) J.-B. Baudin, I. Bkouche-Waksman, S. A. Julia, C. Pascard and Y. Wang, *Tetrahedron*, **47,** 3353 (1991).
4. a) C. J. M. Stirling, *Chem. Commun.*, 131 (1967); b) S. Braverman and H. Mechoulam, *Tetrahedron*, **30,** 3883 (1974); c) M. Conrads and J. Mattay, *Synthesis*, 11 (1991).
5. L. Brandsma and H. D. Verkruijsse, *Synthesis of acetylenes, allenes and cumulenes* (Elsevier, 1981).
6. S. Braverman, in: *The Chemistry of Sulfones and Sulfoxides*, Eds. S. Patai, Z. Rappoport, C. J. M. Stirling, (John Wiley & Sons, Chichester, 1988), Chs. 13 and 14.
7. a) B. Corbel, J.-P. Paugam, M. Dreux and P. Savignac, *Tetrahedron Letters*, **17,** 835 (1976); b) V. Mark, *Mechanisms of Molecular Migrations* (John Wiley & Sons, N. Y. (1969), Vol. 2, p. 319; c) E. V. Bajudina, D. N. Sadkova and I. A. Nuretdinov, *Zh. Obshch. Khim.*, **51,** 957 (1981); d) Ch. M. Angelov and O. Dahl, *Tetrahedron Letters*, **24,** 1643 (1983); e) A. A. Shturlina, E. V. Bajudina, D. N. Sadkova and I. A. Nuretdinov, *Zh. Obshch. Khim*, **57,** 803 (1987); f) A. D. Salimbaeva,

B. J. Jiembaev, S. K. Tukanova and B. M. Butin, *Zh. Obshch. Khim*, **60,** 1008 (1990).
8. C. R. Johnson, in: *Comprehensive Organic Chemistry*, Eds. D. Barton and W. David Ollis (Pergamon Press, 1979), Vol. 3.
9. N. D. Epiotis, R. L. Yates, F. Bernardi and S. Wolfe, *J. Am. Chem. Soc.*, **98,** 5435 (1976) and references cited therein.
10. L. J. Bellamy, *Advances in Infrared Group Frequencies* (Methuen & Co., Bungay, Sulfork, 1968).
11. R. A. Nyqvist, *Spectrochim. Acta*, **19,** 713 (1963).
12. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds* (John Wiley & Sons, 1974).
13. J.-H. Youn and R. Herrman, *Tetrahedron Letters*, **27,** 1493 (1986).