Reactions of sulfenamides with alkynes in the presence of phosphorus(v) oxohalides

N. V. Zyk, E. K. Beloglazkina, M. A. Belova, and N. S. Zefirov*

Department of Chemistry, M. V. Lomonosov Moscow State University,
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 0290. E-mail: SMA@org.chem.msu.ru

The reactions of alkynes with arylsulfenamides activated with phosphorus oxohalides giving rise to aryl β-halovinyl sulfides were investigated. The reactions with acetylene, oct-1-yne, and oct-4-yne are *trans*-stereospecific, whereas the reaction with phenylacetylene afforded a mixture of *cis*- and *trans*-addition products. The addition to unsymmetrical alkynes yielded a mixture of Markovnikoff and anti-Markovnikoff isomers whose ratio depends on the solvent. Products of addition to oct-1-yne in the presence of catalytic amounts of acids underwent isomerization.

Key words: arylsulfenamides, phosphorus(v) oxohalides, alkynes, aryl β-halovinyl sulfides, sulfenylation, isomerization.

Sulfenylation of unsaturated compounds has long been used in organic synthesis. Generally, the electrophilic addition of sulfur(II) compounds to alkenes proceeds in high yields. The mechanism of this reaction has been studied in detail in a series of works, whereas the electrophilic addition to alkynes has been investigated to a lesser extent. The use of sulfenyl chlorides,[1—14] thiols in the presence of metal-complex catalysts,[15,16] sulfur dichloride,[17] *O*-sulfenyl arylsulfonates,[18] complexes of arenesulfenanilides with boron trifluoride,[19—25] and arylsulfenamides activated by sulfuric anhydride[26] as sulfenylating reagents was described in the literature.

Nowadays, the addition of sulfenyl chlorides to unsaturated compounds is commonly used for chlorosulfenylation of the latter. The reactions of sulfenyl chlorides with unsaturated systems have been thoroughly studied. Thus, the reaction mechanism, the kinetics, and the stereochemistry of the process were described in detail.[27,28] However, this procedure has a number of substantial drawbacks, *viz.*, sulfenyl chlorides are unstable compounds and decompose to form the corresponding disulfides. In addition, sulfenyl chlorides react slowly with olefin systems and even more slowly with acetylenic systems. The addition of sulfenyl bromides at multiple bonds does not necessarily give the desired results due to the fact that degradation of sulfenyl bromide to form disulfide proceeds more rapidly than its addition to the multiple bond.[29,30] Because of this, no sufficiently convenient and simple procedures for the preparation of β-bromovinyl sulfides are available.

Presently, the use of weak electrophiles, for example, of esters and amides of sulfenic acids activated by Lewis acids, as sulfenylating reagents is acquiring increasing importance. Previously,[31] we have developed a new procedure for halosulfenylation of olefins with sulfenamides activated by phosphorus oxohalides ($POCl_3$ or $POBr_3$). This procedure has a number of obvious advantages, *viz.*, sulfenamides are stable compounds, phosphorus oxohalides are readily accessible, and the yields are nearly quantitative. As part of our continuing studies, in the present work we investigated the reactions of sulfenamides, which were activated by phosphorus oxohalides, with a series of acetylenic substrates.

Results and Discussion

We assume the following mechanism of activation of sulfenamides. Initially, $POCl_3$ (or $POBr_3$) acts as Lewis acid and attacks the nitrogen atom of sulfenamide. Then the phosphorus—halogen bond is cleaved and the resulting intermediate reacts with the unsaturated substrate to form aryl β-halovinyl sulfides (**1—17**).

It should be noted that the intermediate is, apparently, neither a pure episulfonium ion nor sulfurane. These two structures reflect only the possible limiting forms of the intermediate whose structure may depend on the solvent, the substituents at the multiple bond of the substrate, and the structure of the initial sulfenamide.

The data on the yields of the reaction products and the isomer ratios are given in Table 1.

As expected, the rates of the addition of sulfenamides to acetylenes are substantially lower than the rates of the addition to olefins. Thus, the reactions involving olefins were completed in 15—20 min at −40 °C, whereas the reactions with acetylenes proceeded at room temperature and the reaction time varied from 1.5 to 24 h depending on the structures of the substrate and the reagent.

Acceptor substituents at the triple bond cause a decrease in the reaction rate and in the yields of the products in contrast to donor substituents, which improve these characteristics. Thus, the reactions with phenylacetylene were completed in 20—24 h, whereas

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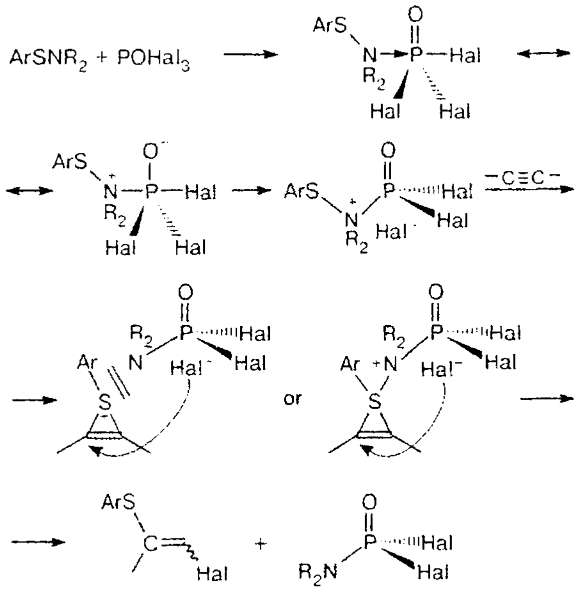


1—17

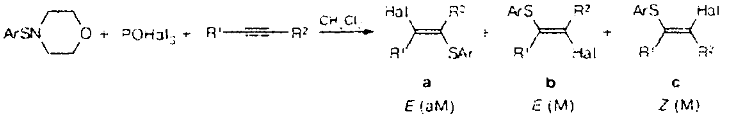
the reactions with oct-4-yne containing two donor substituents at the multiple bond were completed in 1—1.5 h. The reaction with acetylene proceeded rather slowly (3—3.5 h) and is characterized by a low yield compared to those obtained in the reactions with substituted alkynes.

In the case of sulfenamides containing acceptor substituents in the benzene ring in the *ortho* and *para* positions with respect to the sulfur atom, the reaction rates and the yields of the products were higher than those achieved in the cases of phenyl- and tolylsulfenamides.

It should be noted that the main reaction was accompanied by the side process of conversion of sulfenamide into disulfide, which also affected the yields of the reaction products. Thus, the reactions of sulfenamide, phosphorus oxohalides, and alkynes taken in an equimolar ratio afforded aryl β-halovinyl sulfides in approximately 30% yields, and the reaction mixtures always contained the unconsumed alkyne because a portion of sulfenamide decomposed to disulfide. We succeeded in increasing the yields of the halosulfenylation products to 65—90% by using a 1.5-fold excess of a sulfenamide—phosphorus oxohalide mixture in the case of substituted alkynes. To the contrary, the reaction with acetylene was carried out with an excess of alkyne and, hence, the yield was 16% (with respect to sulfenamide).

Most of the published data are indicative of the *trans*-addition of sulfenyl chlorides,[1,3–5,8] sulfur dichloride,[17] *O*-sulfenyl arylsulfonates,[18] sulfenanilides activated with BF$_3$,[19,21] and sulfenamides activated with SO$_3$[26] to acetylenes. However, some researchers reported that they obtained products of *cis*-addition of aryl

Table 1. Yields of the products of the reactions of sulfenamides with alkynes in the presence of phosphorus(V) oxohalides



Alkyne		POHal$_3$, Hal	Sulfenamide, Ar	Product	Total yield (%)	Ratio of the products (%)		
R^1	R^2					**a**	**b**	**c**
H	Ph	Cl	4-O$_2$NC$_6$H$_4$	**1**	86	70	30	—
				1	32*	88	12	—
			2-O$_2$NC$_6$H$_4$	**2**	65	56	44	—
			Ph	**3**	25	15	65	20
		Br	4-O$_2$NC$_6$H$_4$	**4**	82	30	51	19
			2-O$_2$NC$_6$H$_4$	**5**	88	88	12	—
			Ph	**6**	33	51	33	16
H	C$_6$H$_{13}$	Cl	4-O$_2$NC$_6$H$_4$	**7**	70	79	21	—
			2-O$_2$NC$_6$H$_4$	**8**	90	70	30	—
		Br	4-O$_2$NC$_6$H$_4$	**9**	17**	18	82	—
			2-O$_2$NC$_6$H$_4$	**10**	88	67	33	—
C$_3$H$_7$	C$_3$H$_7$	Cl	4-O$_2$NC$_6$H$_4$	**11**	70	100	—	—
			2-O$_2$NC$_6$H$_4$	**12**	77	100	—	—
			Ph	**13**	27	100	—	—
			4-H$_3$CC$_6$H$_4$	**14**	26	100	—	—
		Br	4-O$_2$NC$_6$H$_4$	**15**	67	100	—	—
			2-O$_2$NC$_6$H$_4$	**16**	67	100	—	—
H	H	Cl	4-O$_2$NC$_6$H$_4$	**17**	16	100	—	—

Note: M are Markovnikoff addition products and aM are anti-Markovnikoff addition products.

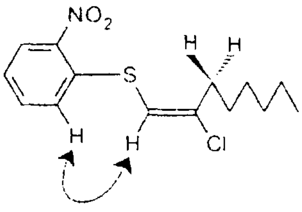
* EtOAc was used as the solvent.

** Products **d** and **e** were obtained along with products **a** and **b** (see the text).

sulfenyl chlorides to phenylacetylene[6,7] and that the *trans*-addition products were isomerized to the corresponding *cis*-addition products upon boiling in benzene[7] or in the presence of the initial sulfenyl chloride.[14] We suggested that in the case under study, the addition of sulfenamides activated with phosphorus oxohalides to acetylenes proceeded *trans*-stereospecifically (which has been unambiguously confirmed for olefins[31]).

In the case of acetylene, the *trans* configuration of the addition product can be judged from the spin-spin coupling constants for olefin protons in the ^{1}H NMR spectrum. Thus, these constants are 13.2 and 6—12 Hz for 1-chloro-2-(*p*-nitrophenylthio)ethylene **4a** and the *cis* isomer, respectively.[32]

To obtain more convincing evidence for the *trans* configurations of the products, which we obtained in the reactions with substituted acetylenes, we performed the nuclear Overhauser effect experiment for a mixture of isomeric β-chloro-(*o*-nitrophenylthio)oct-1-enes **8a** and **8b**. Thus, irradiation of the olefin proton in **8b** (at δ 6.29) led to an increase in the intensity of the signal for the aromatic proton in the *ortho* position with respect to the vinylthio group (at δ 8.22), whereas the intensities of the signals for the allylic protons remained unchanged.



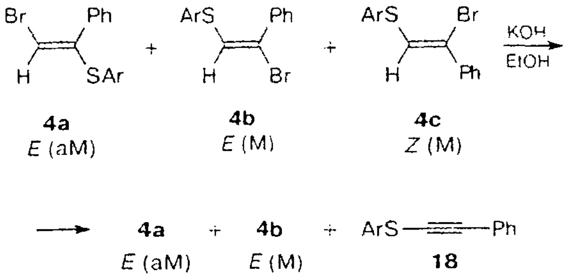
E adduct **8b**

This result indicates that the olefin proton in **8b** is spatially remote from the alkyl radical and is located in proximity to the thioaryl substituent, which supports our suggestion that the products have *trans* configurations.

In the case of unsymmetrical substrates, two regioisomers, *viz.*, Markovnikoff and anti-Markovnikoff addition products, can form. Actually, the ^{1}H NMR spectra of the products of the reactions of oct-1-yne with sulfenamides in the presence of $POCl_3$ or $POBr_3$ have two singlets at δ 6.0—7.0 with different intensities whose chemical shifts differ by 0.2—0.5 ppm. These signals correspond to the olefin protons of two isomers. The assignment of the signals was made based on the published data.[8,10]

The reactions with oct-1-yne gave anti-Markovnikoff (*E*)-isomers as the major products (except for products **9a** and **9b**; see below). This fact is not surprising because it is known that anti-Markovnikoff products are formed under conditions of kinetic control and these products can undergo isomerization upon storage to form more thermodynamically stable Markovnikoff products.[33] However, we did not observe isomerization of the reaction products upon their storage for two months at 20 °C as well as on boiling in chloroform.

The reactions with phenylacetylene afforded *cis* isomers of aryl β-halovinyl sulfides along with the *trans*-addition products. This fact is in good agreement with the published data on the formation of the *cis*-addition products in the reactions of sulfenyl halides with phenylacetylene.[5–7,14] Of four possible addition products, only Markovnikoff *cis*-addition product **4c** can readily eliminate HHal. To establish the structures of the isomeric compounds, a mixture of **4a—c** was treated with an alcoholic solution of alkali. According to the data of ^{1}H NMR and IR spectroscopy, the reaction mixture obtained after such treatment did not contain compound **4c** and contained a new compound bearing the C≡C fragment. We assigned structure **18** to the latter compound. Apparently, the insignificant decrease in the content of isomer **4b** is associated with the possibility of *cis*-elimination of HBr from this compound.

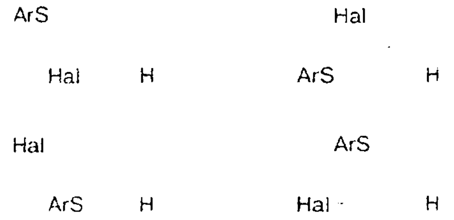


Ar = 4-O_2N-C_6H_4

With the aim of studying the effect of the solvent on the ratio between the Markovnikoff and anti-Markovnikoff isomers, we carried out the reaction of *p*-nitrophenylthiomorpholine with phenylacetylene in ethyl acetate in the presence of $POCl_3$. In this case, the **1a** : **1b** isomer ratio changed to 88 : 12, which is in good agreement with the published data on the effect of the solvent on the isomer ratio in the case of addition of sulfenyl chlorides to acetylenes. This suggests that the ratio between the Markovnikoff and anti-Markovnikoff products in the reaction under consideration depends on the solvating ability of the solvent, as in the case of sulfenyl chlorides.[4,5]

Isomerization of products of addition of sulfenamides to oct-1-yne. Chromatographic separation of the products of the reaction between *p*-nitrophenylthiomorpholine and oct-1-yne in the presence of $POBr_3$ gave two fractions. One of these fractions contained a mixture of 1,2-addition products, *viz.*, (*E*)-1-bromo-2-(*p*-nitrophenylthio)oct-1-ene (**9a**) and (*E*)-2-bromo-1-(*p*-nitrophenylthio)oct-1-ene (**9b**), the Markovnikoff isomer prevailing. To the contrary, the inverse ratios of isomers **a** and **b** were observed in all other reactions of sulfenamides with oct-1-yne.

The ^{1}H NMR spectrum of the second fraction has a triplet at δ 6.6 with the intensity of 1.0 H, a triplet at δ 6.3 with the intensity of 0.33 H, two singlets (at δ 4.11 and 4.09) with the total intensity of 3.02 H, and three groups of multiplet signals in the high-field region along with signals for the protons of the *p*-nitro-substituted benzene ring. The triplets at δ 6.6 and 6.3 belong to the olefin protons of two isomers **9d** and **9e**, respectively. The shape of the signal and the spin-spin coupling constant (7.5 Hz) are indicative of the presence of the CH$_2$ group adjacent to the double bond. The singlets in the region of δ 4.10 belong, apparently, to the protons at the carbon atoms bearing substituents (—SAr or —Br), the ratio between the intensities of these signals and the integral intensity of the signals for the olefin protons being 2 : 1. In addition, the absence of splitting of the two-proton signals is indicative of the absence of vicinal protons. Based on the above-considered data, the following four structures **9d,e** may be proposed:

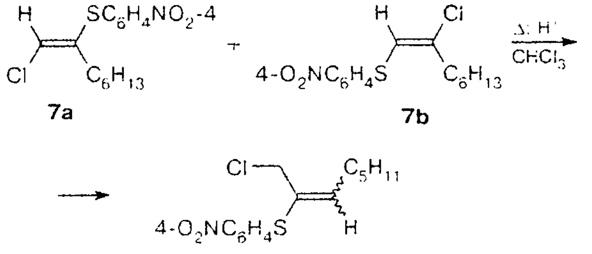


We suggested that the double bond in the products of 1,2-addition to oct-1-yne that initially formed migrated under the action of small amounts of acids, which were present as impurities in phosphorus oxobromide. As a result, the reaction under consideration afforded four rather than two isomeric bromosulfides as the final products (Scheme 1).

To verify this suggestion, we decided to find out whether other 1,2-addition products, for example, isomeric chloro(*p*-nitrophenylthio)oct-1-enes **7a** and **7b**, also undergo isomerization. A mixture of **7a** and **7b** (taken in a ratio of 79 : 21) was refluxed in chloroform for 3 h after which no compounds other than the initial reagents were detected in the solution by TLC. However, new compounds were found (by TLC) in the reaction mixture within 30 min after the addition of catalytic amounts of *p*-toluenesulfonic acid to a solution of **7a** and **7b** in chloroform.

Based on the data of ^{1}H NMR spectroscopy, it can be concluded that refluxing of a mixture of compounds **7a** and **7b** in chloroform in the presence of *p*-toluenesulfonic acid afforded compounds **7d** and **7e**, which are structurally similar to compounds **9d** and **9e** isolated in the reaction of (*p*-nitrophenylthio)morpholine with oct-1-yne in the presence of POBr$_3$. This fact provides evidence in favor of the fact that the double bond in products of 1,2-addition to oct-1-yne migrates under the action of catalytic amounts of acids.

Based on the intensity ratio of the signals in the ^{1}H NMR spectrum, it was established that compounds **7a,b,d,e** were present in the mixture in a ratio of 9 : 20 : 42 : 29. To put it differently, the total amount of the resulting products **7d** + **7e** (71%) was exactly equal (±1%) to the amount of compound **7a** consumed (79 − 9 = 70%), whereas the amount of the initial component **7b** remained unchanged (±1%), *i.e.*, exclusively the anti-Markovnikoff *E*-isomer underwent isomerization resulting in a mixture of 1-chloro-2-(*p*-nitrophenylthio)oct-2-enes. This process can be described by Scheme 2.

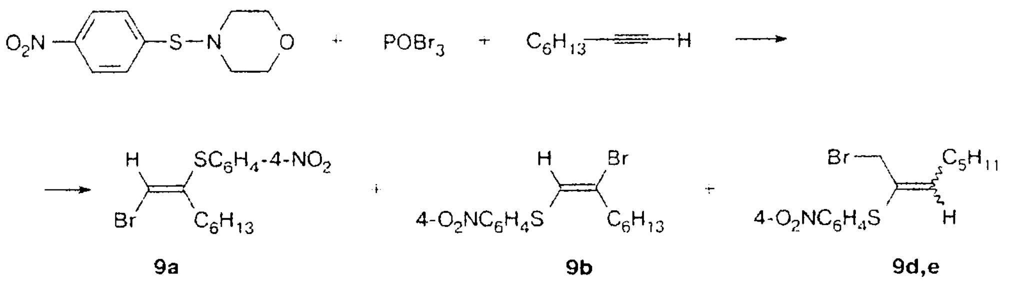


7a **7b** **7d,e**

The signals in the ^{1}H NMR spectra were more accurately correlated with the structures of the pair of compounds **9d** and **9e** and the pair of **7d** and **7e** based on the published data on the chemical shifts of the olefin protons in trisubstituted ethylenes. The literature data along with the data for compounds **7d,e** and **9d,e** are given in Table 2.

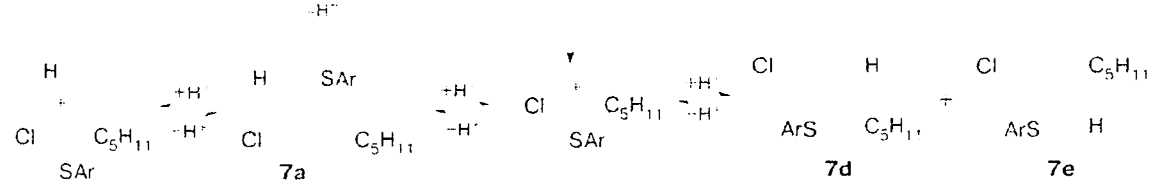
These data indicate that the signal for the proton in the *trans* position with respect to the substituent containing the lone electron pair is observed at lower field than the signal for the proton in the *cis* position with respect to this substituent. By analogy, the assignment made by us seems to be more probable. Thus, the signal for the olefin proton in compounds **9d** and **7d** containing the proton in the *trans* position with respect to the arylthio group should be observed at lower field than the signal for the olefin proton in compounds **9e** and **7e**

Scheme 1



9a **9b** **9d,e**

Scheme 2



Ar = 4-O_2N-C_6H_4

containing the proton in the *cis* position with respect to the arylthio group.

The reaction discovered by us is most similar to the migration of the double bond in products of addition of thiols to terminal alkynes in the presence of metal-complex catalysts reported in 1999.[16] Thus, the reactions of alkynes containing the propargylic hydrogen atoms with thiophenol in the presence of the palladium catalyst ($PdCl_2(PhCN)_2$) afforded primarily Markovnikoff addition products, *viz.*, 2-(phenylthio)alk-1-enes. In the reactions with the complex of thiophenol using the catalyst $Pd(SPh)Cl(PhSH)_m$ (m = 1 or 2), alkynes underwent isomerization through the carbocationic intermediate to form 2-(phenylthio)alk-2-ene.

Therefore, the reactions of arylsulfenamides with alkynes in the presence of phosphorus oxohalides can serve as a convenient procedure for the synthesis of aryl β-halovinyl sulfides. The migration of the double carbon—carbon double in the reaction products opens up new synthetic possibilities.

Experimental

The ^1H NMR spectra were recorded on a Varian VXR-400 instrument operating at 400 MHz. The ^{13}C NMR spectra were measured on a Varian-XR-400 instrument operating at 100 MHz. The IR spectra were obtained on a UR-20 instrument in thin films. The melting points were determined in open capillaries on a block. The melting and boiling points were not corrected.

Reactions of sulfenamides with alkynes in the presence of phosphorus(v) oxohalides. A solution of phosphorus(v) oxohalide (1.5 mmol) in anhydrous CH_2Cl_2 was slowly added with intense stirring to a solution of sulfenamide (1.5 mmol) in the same solvent at –20 °C and the reaction mixture was stirred for 10 min. Then a solution of alkyne (1 mmol) in anhydrous CH_2Cl_2 was slowly added and the mixture was stirred until alkyne was completely consumed (the course of the reaction was monitored by TLC on Silufol plates with a fixed silica gel layer). The solvent was removed on a rotary evaporator and the residue was separated on a chromatography column with SiO_2 (a 1 : 3 $CHCl_3$—light petroleum mixture as the eluent).

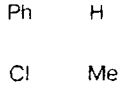
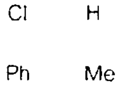
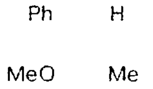
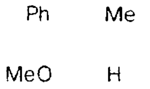
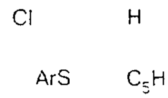
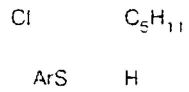
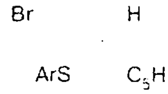
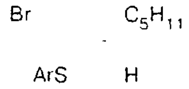
Mixture of 1-chloro-(*E*)-2-(*p*-nitrophenylthio)-2-phenylethylene (1a) and 1-chloro-(*E*)-2-(*p*-nitrophenylthio)-1-phenylethylene (1b). R_f = 0.22 ($CHCl_3$—light petroleum, 1 : 3). ^1H NMR ($CDCl_3$), δ: 8.04 (d, 2 H, **1a**: 4-$O_2N-C_6H_4$, J = 9.2 Hz); 7.96 (d, 2 H, **1b**: 4-$O_2N-C_6H_4$, J = 9.2 Hz); 7.58—7.53 (m, 2 H, **1a**: 4-$O_2N-C_6H_4$); 7.51 (d, 2 H, **1b**: 4-$O_2N-C_6H_4$, J = 9.2 Hz); 7.40—7.20 (m, **1a** + **1b**: Ph); 6.96 (s, 1 H, **1a**: HC=); 6.68 (s, 1 H, **1b**: HC=). IR (thin film), ν/cm^{-1}: 1340, 1520 (—NO_2); 1605 (C=C). For the mixture, found (%): C, 57.90; H, 3.35. $C_{14}H_{10}ClNO_2S$. Calculated (%): C, 57.63; H, 3.45.

Mixture of 1-chloro-(*E*)-2-(*o*-nitrophenylthio)-2-phenylethylene (2a) and 1-chloro-(*E*)-2-(*o*-nitrophenylthio)-1-phenylethylene (2b). R_f = 0.29 ($CHCl_3$—light petroleum, 1 : 3). ^1H NMR ($CDCl_3$), δ: 8.16 (d, 1 H, **2a**: 2-$O_2N-C_6H_4$, J = 9.3 Hz); 8.08 (d, 1 H, **2b**: 2-$O_2N-C_6H_4$, J = 9.3 Hz); 7.64 (t, 1 H, **2a**: 2-$O_2N-C_6H_4$, J = 9.3 Hz); 7.59 (t, 1 H, **2a**: 2-$O_2N-C_6H_4$, J = 9.1 Hz); 7.56—7.34 (m, 10 H, **2a** + **2b**: Ph); 7.30 (d, 1 H, **2b**: 2-$O_2N-C_6H_4$, J = 9.1 Hz); 7.27 (t, 1 H, **2b**: 2-$O_2N-C_6H_4$, J = 9.3 Hz); 7.18—7.12 (m, 2 H, **2a** + **2b**: 2-$O_2N-C_6H_4$); 7.06 (s, 1 H, **2a**: HC=); 6.64 (s, 1 H, **2b**: HC=). ^{13}C NMR ($CDCl_3$), δ: 135.32—135.17 (2 C, **2a** + **2b**: SC(arom)); 134.32; 134.20—134.06 (2 C); 133.85—133.25 (2 C); 129.47 (2 C); 129.31; 129.08—128.76 (5 C); 128.48—128.45 (2 C); 128.24—128.16 (4 C); 126.38—126.03 (2 C); 125.94—125.72 (4 C); 124.89; 118.97. IR (thin film), ν/cm^{-1}: 1340, 1520 (—NO_2); 1600 (C=C). For the mixture, found (%): C, 57.44; H, 3.38. $C_{14}H_{10}ClNO_2S$. Calculated (%): C, 57.63; H, 3.45.

Mixture of 1-chloro-(*E*)-2-phenyl-2-phenylthioethylene (3a), 1-chloro-(*E*)-1-phenyl-2-phenylthioethylene (3b), and 1-chloro-(*Z*)-1-phenyl-2-phenylthioethylene (3c). R_f = 0.35 ($CHCl_3$—light petroleum, 1 : 3). ^1H NMR ($CDCl_3$), δ: 7.28—7.24 (m, 15 H, **3a** + **3b** + **3c**: SC_6H_5); 7.20—7.12 (m, 15 H, **3a** + **3b** + **3c**: Ph); 6.68 (s, 1 H, **3a**: HC=); 6.56 (s, 1 H, **3b**: HC=); 6.52 (s, 1 H, **3c**: HC=).

Mixture of (*E*)-1-bromo-2-(*p*-nitrophenylthio)-2-phenylethylene (4a), (*E*)-1-bromo-2-(*p*-nitrophenylthio)-1-phenylethylene (4b), and (*Z*)-1-bromo-2-(*p*-nitrophenylthio)-1-phenylethylene (4c). R_f = 0.29 ($CHCl_3$—light petroleum, 1 : 3).

Table 2. Chemical shifts of the protons of trisubstituted ethylenes

Compound	δ	Compound	δ
	6.09*		5.95*
	5.22*		4.67*
 **7d**	6.60	 **7e**	6.30
 **9d**	6.65	 **9e**	6.36

* The data published previously.[9]

^{1}H NMR (CDCl$_3$), δ: 8.13 (d, 2 H, **4c**: 4-O$_2$N—C$_6$H$_4$, J = 8.7 Hz); 7.98 (d, 2 H, **4a**: 4-O$_2$N—C$_6$H$_4$, J = 8.7 Hz); 7.95 (d, 2 H, **4b**: 4-O$_2$N—C$_6$H$_4$, J = 8.7 Hz); 7.57—7.50 (m, 4 H, **4b** + **4c**: 4-O$_2$N—C$_6$H$_4$); 7.48 (d, 2 H, **4a**: 4-O$_2$N—C$_6$H$_4$, J = 8.5 Hz); 7.40—7.33 (m, 10 H, **4b** + **4c**: Ph); 7.28—7.24 (m, 5 H, **4a**: Ph); 7.13 (s, 1 H, **4a**, HC=); 7.03 (s, 1 H, **4b**: HC=); 6.89 (s, 1 H, **4c**: HC=). IR (thin film), ν/cm^{-1}: 1345, 1520 (—NO$_2$), 1605 (C=C).

Mixture of (*E*)-1-bromo-2-(*o*-nitrophenylthio)-2-phenylethylene (5a), and (*E*)-1-bromo-2-(*o*-nitrophenylthio)-1-phenylethylene (5b), R_f = 0.26 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.31 (d, 1 H, **5b**: 2-O$_2$N—C$_6$H$_4$, J = 8.9 Hz); 8.16 (d, 1 H, **5a**: 2-O$_2$N—C$_6$H$_4$, J = 8.9 Hz); 7.62 (t, 1 H, **5a**: 2-O$_2$N—C$_6$H$_4$, J = 8.9 Hz); 7.55 (t, 1 H, **5b**: 2-O$_2$N—C$_6$H$_4$, J = 8.9 Hz); 7.52—7.34 (m, 10 H, **5a** + **5b**: Ph); 7.31—7.12 (m, 4 H, **5a** + **5b**: 2-O$_2$N—C$_6$H$_4$); 6.88 (s, 1 H, **5a**: HC=); 6.65 (s, 1 H, **5b**: HC=). IR (thin film), ν/cm^{-1}: 1340, 1525 (—NO$_2$), 1600 (C=C).

Mixture of (*E*)-1-bromo-2-phenyl-2-phenylthioethylene (6a), (*E*)-1-bromo-1-phenyl-2-phenylthioethylene (6b), and (*Z*)-1-bromo-1-phenyl-2-phenylthioethylene (6c), R_f = 0.33 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 7.29—7.13 (m, 15 H, **6a** + **6b** + **6c**: SC$_6$H$_5$); 7.10—7.03 (m, 15 H, **6a** + **6b** + **6c**: Ph); 6.87 (s, 1 H, **6a**: HC=); 6.67 (s, 1 H, **6b**: HC=); 6.56 (s, 1 H, **6c**: HC=).

Mixture of 1-chloro-(*E*)-2-(*p*-nitrophenylthio)oct-1-ene (7a) and 2-chloro-(*E*)-1-(*p*-nitrophenylthio)oct-1-ene (7b), R_f = 0.47 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.12 (d, 4 H, **7a** + **7b**: 4-O$_2$N—C$_6$H$_4$, J = 9.2 Hz); 7.32 (d, 4 H, **7a** + **7b**: 4-O$_2$N—C$_6$H$_4$, J = 9.2 Hz); 6.62 (s, 1 H, **7a**: HC=); 6.32 (s, 1 H, **7b**: HC=); 2.61 (t, 2 H, **7b**: HC(3), J = 7.1 Hz); 2.40 (t, 2 H, **7a**: HC(3), J = 7.2 Hz); 1.60 (m, 2 H, **7b**: HC(4)); 1.50 (m, 2 H, **7a**: HC(4)); 1.35—1.20 (m, 12 H, **7a** + **7b**: HC(5), HC(6), HC(7)); 0.85 (t, 6 H, **7a** + **7b**: HC(8), J = 7.1 Hz). IR (thin film), ν/cm^{-1}: 1340, 1520 (—NO$_2$); 1605 (C=C). For the mixture, found (%): C, 56.34; H, 6.40. C$_{14}$H$_{18}$ClNO$_2$S. Calculated (%): C, 56.09; H, 6.05.

Mixture of 1-chloro-(*E*)-2-(*o*-nitrophenylthio)oct-1-ene (8a) and 2-chloro-(*E*)-1-(*o*-nitrophenylthio)oct-1-ene (8b), R_f = 0.44 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.22 (d, 1 H, **8b**: 2-O$_2$N—C$_6$H$_4$, J = 9.4 Hz); 8.20 (d, 1 H, **8a**: 2-O$_2$N—C$_6$H$_4$, J = 9.4 Hz); 7.57 (t, 1 H, **8b**: 2-O$_2$N—C$_6$H$_4$, J = 9.4 Hz); 7.53 (t, 1 H, **8a**: 2-O$_2$N—C$_6$H$_4$, J = 9.4 Hz); 7.41 (t, 1 H, **8a**: 2-O$_2$N—C$_6$H$_4$, J = 9.4 Hz); 7.32—7.26 (m, 3 H, **8a** + **8b**: 2-O$_2$N—C$_6$H$_4$); 6.71 (s, 1 H, **8a**: HC=); 6.29 (s, 1 H, **8b**: HC=); 2.69 (t, 2 H, **8b**: HC(3), J = 7.1 Hz); 2.39 (t, 2 H, **8a**: HC(3), J = 7.1 Hz); 1.60 (m, 2 H, **8b**: HC(4)); 1.50 (m, 2 H, **8a**: HC(4)); 1.35—1.20 (m, 12 H, **8a** + **8b**: HC(5), HC(6), HC(7)); 0.85 (t, 6 H, **8a** + **8b**: HC(8), J = 6.9 Hz). ^{13}C NMR (CDCl$_3$), δ: 146.17; 135.94; 135.32; 133.71; 133.45 (2 C); 128.42 (2 C); 127.86; 126.68; 126.12; 126.07; 125.62 (2 C); 125.49; 116.50; 31.66; 31.44 (2 C); 28.75 (2 C); 28.22; 27.37; 27.22; 22.48 (2 C); 13.99 (2 C). IR (thin film), ν/cm^{-1}: 1340, 1530 (—NO$_2$), 1600 (C=C). For the mixture, found (%): C, 57.23; H, 6.00. C$_{14}$H$_{18}$ClNO$_2$S. Calculated (%): C, 56.08; H, 6.05.

Mixture of (*E*)-1-bromo-2-(*p*-nitrophenylthio)oct-1-ene (9a) and (*E*)-2-bromo-1-(*p*-nitrophenylthio)oct-1-ene (9b). R_f = 0.46 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.15 (d, 4 H, **9a** + **9b**: 4-O$_2$N—C$_6$H$_4$, J = 8.7 Hz); 7.34 (d, 4 H, **9a** + **9b**: 4-O$_2$N—C$_6$H$_4$, J = 8.7 Hz); 6.77 (s, 1 H, **9a**: HC=); 6.55 (s, 1 H, **9b**: HC=); 2.69 (t, 2 H, **9a**: HC(3), J = 7.5 Hz); 2.46 (t, 2 H, **9b**: HC(3), J = 7.2 Hz); 1.63—1.15 (m, 16 H, **9a** + **9b**: HC(4), HC(5), HC(6), HC(7)); 0.85 (t, 6 H, **9a** + **9b**: HC(8), J = 6.2 Hz).

Mixture of (*Z*)-1-bromo-2-(*p*-nitrophenylthio)oct-2-ene (9d) and (*E*)-1-bromo-2-(*p*-nitrophenylthio)oct-2-ene (9e). R_f = 0.28 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.11 (d, 4 H, **9d** + **9e**: 4-O$_2$N—C$_6$H$_4$, J = 9.1 Hz); 7.31 (d, 4 H, **9d** + **9e**: 4-O$_2$N—C$_6$H$_4$, J = 9.1 Hz); 6.65 (t, 1 H, **9e**: HC=, J = 7.5 Hz); 6.36 (t, 1 H, **9d**: HC=, J = 7.5 Hz); 4.11 (s, 2 H, **9e**: H$_2$C(1)); 4.08 (s, 2 H, **9d**: H$_2$C(1)); 2.30 (m, 4 H, **9d** + **9e**: =C—CH$_2$); 1.56—1.22 (m, 12 H, **9d** + **9e**: HC(5), HC(6), HC(7)); 0.94—0.85 (m, 6 H, **9d** + **9e**: HC(8)). IR (thin film), ν/cm^{-1}: 1340, 1520 (—NO$_2$), 1600 (C=C). For the mixture of **9d** and **9e**, found (%): C, 47.87; H, 5.49. C$_{14}$H$_{18}$BrNO$_2$S. Calculated (%): C, 48.83; H, 5.27.

Mixture of (*E*)-1-bromo-2-(*o*-nitrophenylthio)oct-1-ene (10a) and (*E*)-2-bromo-1-(*o*-nitrophenylthio)oct-1-ene (10b). R_f = 0.57 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.22 (d, 1 H, **10b**: 2-O$_2$N—C$_6$H$_4$, J = 8.8 Hz); 8.19 (d, 1 H, **10a**: 2-O$_2$N—C$_6$H$_4$, J = 8.9 Hz); 7.57 (t, 1 H, **10b**: 2-O$_2$N—C$_6$H$_4$, J = 8.3 Hz); 7.53 (t, 1 H, **10a**: 2-O$_2$N—C$_6$H$_4$, J = 8.1 Hz); 7.42 (d, 1 H, **10a**: 2-O$_2$N—C$_6$H$_4$, J = 8.3 Hz); 7.33—7.26 (m, 3 H, **10a** + **10b**: 2-O$_2$N—C$_6$H$_4$); 6.9 (s, 1 H, **10a**: HC=); 6.53 (s, 1 H, **10b**: HC=); 2.78 (t, 2 H, **10b**: HC(3), J = 7.2 Hz); 2.48 (t, 2 H, **10a**: HC(3), J = 7.1 Hz); 1.59 (m, 2 H, **10b**: HC(4)); 1.49 (m, 2 H, **10a**: HC(4)); 1.33—1.19 (m, 12 H, **10a** + **10b**: HC(5), HC(6), HC(7)); 0.84 (t, 6 H, **10a** + **10b**: HC(8), J = 7.2 Hz). IR (thin film), ν/cm^{-1}: 1340, 1530 (—NO$_2$), 1600 (C=C). For the mixture, found (%): C, 47.76; H, 5.12. C$_{14}$H$_{18}$BrNO$_2$S. Calculated (%): C, 48.83; H, 5.27.

4-Chloro-(*E*)-5-(*p*-nitrophenylthio)oct-4-ene (11). R_f = 0.36 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.12 and 7.24 (both d, each 2 H, 4-O$_2$N—C$_6$H$_4$, J = 8.8 Hz); 2.72 and 2.44 (both t, each 2 H, HC(3), HC(6), J = 7.4 Hz); 1.61 and 1.55 (both m, each 2 H, HC(2), HC(7)); 0.89 (t, 6 H, HC(1), HC(8), J = 7.2 Hz). ^{13}C NMR (CDCl$_3$), δ: 146.11 (1 C, SC(arom)); 144.28; 126.76; 126.5 (2 C); 126.43; 124.14 (2 C); 39.24 (1 C, C(6)); 36.76 (1 C, C(3)); 21.21—21.19 (2 C, C(7), C(2)); 13.6—13.16 (2 C, C(8), C(1)). IR (thin film), ν/cm^{-1}: 1340, 1520 (—NO$_2$); 1605 (C=C). Found (%): C, 56.53; H, 6.27. C$_{14}$H$_{18}$ClNO$_2$S. Calculated (%): C, 56.09; H, 6.05.

4-Chloro-(*E*)-5-(*o*-nitrophenylthio)oct-4-ene (12). R_f = 0.56 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.23 and 7.22 (both d, each 1 H, 2-O$_2$N—C$_6$H$_4$, J = 7.8 Hz); 7.52 and 7.27 (both t, each 1 H, 2-O$_2$N—C$_6$H$_4$, J = 7.8 Hz); 2.75 and 2.38 (both t, each 2 H, HC(3), HC(6), J = 7.7 Hz); 1.63 and 1.55 (both m, each 2 H, HC(2), HC(7)); 0.90 and 0.87 (both t, each 3 H, HC(1), HC(8), J = 7.1 Hz). ^{13}C NMR (CDCl$_3$), δ: 145.78 (1 C, SC(arom)); 145.28; 136.48; 133.51; 127.96; 127.74; 126.23; 125.12; 39.09 (1 C, C(6)); 36.99 (1 C, C(3)); 21.21—21.19 (2 C, C(7), C(2)); 13.6—13.18 (2 C, C(8), C(1)). IR (thin film), ν/cm^{-1}: 1340, 1530 (—NO$_2$), 1600 (C=C). Found (%): C, 56.25; H, 6.26. C$_{14}$H$_{18}$ClNO$_2$S. Calculated (%): C, 56.09; H, 6.05.

4-Chloro-(*E*)-5-(phenylthio)oct-4-ene (13). R_f = 0.36 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 7.29—7.14 (m, 5 H, Ph); 2.78 and 2.37 (both t, each 2 H, HC(3), HC(6), J = 7.3 Hz); 1.62 and 1.52 (both m, each 2 H, HC(2), HC(7)); 0.93 and 0.85 (both t, each 3 H, HC(1), HC(8), J = 7.2 Hz). Found (%): C, 65.48; H, 7.39. C$_{14}$H$_{19}$ClS. Calculated (%): C, 65.99; H, 7.52.

4-Chloro-(*E*)-5-(*p*-methylphenylthio)oct-4-ene (14). R_f = 0.29 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 7.90 and 7.39 (both d, each 2 H, 4-H$_3$C—C$_6\underline{H}_4$, J = 8.7 Hz); 2.90 and 2.45 (both t, each 2 H, HC(3), HC(6), J = 7.3 Hz); 2.48 (s, 3 H, $\underline{H}_3$C—C$_6$H$_4$); 1.63 (m, 4 H, HC(2), HC(7)); 1.06 (t, 6 H, HC(1), HC(8), J = 7.2 Hz).

(*E*)-4-Bromo-5-(*p*-nitrophenylthio)oct-4-ene (15). R_f = 0.42 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.12 and 7.24 (both d, each 2 H, 4-O$_2$N—C$_6$H$_4$, J = 8.9 Hz); 2.84 and 2.46 (both t, each 2 H, HC(3), HC(6), J = 7.5 Hz); 1.61—1.50

(m, 4 H, HC(2), HC(7)); 0.89 (t, 6 H, HC(1), HC(8), J = 7.3 Hz). IR (thin film), ν/cm^{-1}: 1340, 1520 (—NO$_2$), 1605 (C=C). Found (%): C, 50.08; H, 6.01. $C_{14}H_{18}BrNO_2S$. Calculated (%): C, 48.83; H, 5.27.

(*E*)-4-Bromo-5-(*o*-nitrophenylthio)oct-4-ene (16). R_f = 0.45 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.23 and 7.21 (both d, each 1 H, 2-$O_2N-C_6H_4$, J = 8.9 Hz); 7.52 and 7.27 (both t, each 1 H, 2-$O_2N-C_6H_4$, J = 8.9 Hz); 2.85 and 2.40 (both t, each 2 H, HC(3), HC(6), J = 7.5 Hz); 1.62 and 1.55 (both m, each 2 H, HC(2), HC(7)); 0.90 and 0.87 (both t, each 3 H, HC(1), HC(8), J = 7.5 Hz). ^{13}C NMR (CDCl$_3$), δ: 138.69 (1 C, SC(arom)); 136.35; 133.56 (2 C); 129.77; 127.99; 126.26; 125.17; 41.42 (1 C, C(6)); 39.95 (1 C, C(3)); 21.96—21.24 (2 C, C(7), C(2)); 13.68—13.10 (2 C, C(8), C(1)). IR, ν/cm^{-1}: 1345, 1530 (—NO$_2$), 1605 (C=C). Found (%): C, 48.69; H, 5.41. $C_{14}H_{18}BrNO_2S$. Calculated (%): C, 48.83; H, 5.27.

1-Chloro-(*E*)-2-(*p*-nitrophenylthio)ethylene (17). R_f = 0.76 (CHCl$_3$—light petroleum, 1 : 3). ^{1}H NMR (CDCl$_3$), δ: 8.16 and 7.36 (both d, each 2 H, 4-$O_2N-C_6H_4$, J = 9.2 Hz); 6.68 and 6.59 (both d, each 1 H, HC=, J = 13.1 Hz). IR (thin film), ν/cm^{-1}: 1340, 1520 (—NO$_2$); 1605 (C=C). Found (%): C, 44.15; H, 2.80. $C_8H_6ClNO_2S$. Calculated (%): C, 44.55; H, 2.78.

Isomerization of 1-chloro-(*E*)-2-(*p*-nitrophenylthio)oct-1-ene (7a) and 2-chloro-(*E*)-1-(*p*-nitrophenylthio)oct-1-ene (7b) in the presence of *p*-toluenesulfonic acid. A mixture of **7a** and **7b** (0.2 g, the ratio was 79 : 21) was dissolved in CHCl$_3$ (10 mL). Then *p*-toluenesulfonic acid (0.05 g) was added to the solution. The mixture was refluxed for 3 h and then passed through a column packed with aluminum oxide. The solvent was removed on a rotary evaporator. A mixture of 1-chloro-(*E*)-2-(*p*-nitrophenylthio)oct-1-ene (**7a**) (9%), 2-chloro-(*E*)-1-(*p*-nitrophenylthio)oct-1-ene (**7b**) (20%), 1-chloro-(*E*)-2-(*p*-nitrophenylthio)oct-1-ene (**7e**) (29%), and 1-chloro-(*Z*)-2-(*p*-nitrophenylthio)oct-2-ene (**7d**) (42%) was obtained. ^{1}H NMR (CDCl$_3$), δ: 8.18—8.08 (m, 8 H, **7a** + **7b** + **7d** + **7e**: 4-$O_2N-C_6H_4$); 7.36—7.27 (m, 8 H, **7a** + **7b** + **7d** + **7e**: 4-$O_2N-C_6H_4$); 6.62 (s, 1 H, **7a**: HC=); 6.61 (t, 1 H, **7e**: HC=, J = 7.2 Hz); 6.36 (t, 1 H, **7d**: HC=, J = 7.8 Hz); 6.32 (s, 1 H, **7b**: HC=); 4.19 (s, 1 H, **7d**: $H_2C(1)$); 4.16 (s, 1 H, **7e**: $H_2C(1)$); 2.61 (t, 2 H, **7b**: HC(3), J = 7.5 Hz); 2.49 (t, 2 H, **7d**: HC(4), J = 7.1); 2.41 (t, 2 H, **7a**: HC(3), J = 7.2 Hz); 2.32 (t, 2 H, **7e**: HC(4), J = 7.5 Hz); 1.63—1.15 (m, 28 H, **7a** + **7b** + **7d** + **7e**: HC(4), HC(5), HC(6), HC(7)); 0.93—0.85 (t, 12 H, **7a** + **7b** + **7d** + **7e**: HC(8), J = 6.2).

Elimination of HBr from a mixture of (*E*)-1-bromo-2-(*p*-nitrophenylthio)-2-phenylethylene (4a), (*E*)-1-bromo-2-(*p*-nitrophenylthio)-1-phenylethylene (4b), and (*Z*)-1-bromo-2-(*p*-nitrophenylthio)-1-phenylethylene (4c). A mixture of **4a—c** (0.25 g, the ratio was 30 : 51 : 19) was refluxed with a 20% alcoholic solution of KOH (10 mL) for 3 h and then poured into ice water. The oil was separated and the aqueous layer was extracted with ether. The oil and the ethereal extracts were combined and dried over KOH. In the ^{1}H NMR spectrum, the signals of compound **4c** disappeared and the intensities of the signals of compound **4b** decreased. IR (thin film), ν/cm^{-1}: 1345, 1530 (—NO$_2$), 1605 (C=C), 2210 (C≡C).

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