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*Dedicated to Full Member of the Russian Academy of Sciences I. P. Beletskaya on occasion of her jubilee*

# Halosulfenylation of Conjugated Dienes with Arylsulfenamides in the Presence of Phosphorus Oxyhalides

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**Abstract**—Electrophilic sulfenylation of cyclic and open-chain conjugated dienes effected by a system arylsulfenamide–phosphorus oxyhalide was investigated. The initially formed adducts of 1,2-halosulfenylation in the course of the reaction and also at storage and chromatograqphic purification on silica gel undergo quantitative isomerization into a mixture of stereoisomeric products of 1,4-addition. The effect of halogen nature and the character of substituents in the benzene ring of arenesulfenamide on the addition rate of sulfenamides activated by phosphorus oxyhalides to open-chain and cyclic conjugated dienes and isomerization rate of the arising 1,2-adducts was examined.

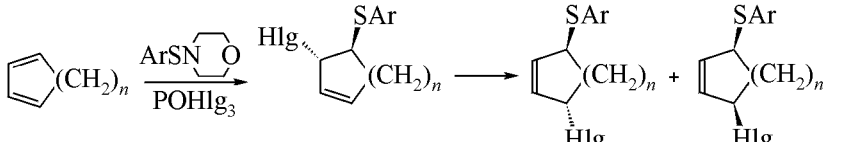
We have formerly described the halosulfenylation of a homoconjugated diene, bicyclo[2.2.1]hepta-2,5-diene, with a system arylsulfenamide–phosphorus oxyhalide [1]. A possibility to prepare various products from the same initial reagents by modification of reaction conditions opens wide synthetic prospects and requires further investigation of this reagent. In this study we examined the addition of arylsulfenamides activated by phosphorus oxyhalides to a number of conjugated dienes: 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 1,3-cyclohexadiene, and 1,3-cyclopentadiene.

The reagent we apply, arylsulfenamide–phosphorus oxychloride, may be regarded as a synthetic equivalent of arylsulfenyl chlorides. The sulfenyl chlorides addition to conjugated dienes is sufficiently well documented [2 8]. On a large number of substituted 1,3-butadienes [5] and on some cyclic diene systems [7, 8] the addition of sulfenyl chlorides was shown to furnish 1,2-adduct. Therewith the addition occurred trans-stereospecifically in keeping with Markownikoff rule. On storage or at heating the 1,2-products isomerized into more stable 1,4-adducts.

On the other hand the system arylsulfenamide–phosphorus oxybromide is a synthetic equivalent of arylsulfenyl bromides whose addition to diene systems is almost unknown.

Our study has shown that the best yields of halosulfenylated products are obtained when excess diene reacts with the system arylsulfenamide–phosphorus oxyhalide (at the ratio diene–sulfenylating agent 1.5 : 1) in $CH_2Cl_2$ at –40°C. Initially formed 1,2-adducts in the course of reaction and also at storage or when submitted to chromatography on silica gel quantitatively isomerize into a mixture of stereoisomeric products of 1,4-addition.

With cyclic dienes the reaction gives rise to a single product of *trans*-1,2-addition across an only double bond.




**Ia–f** ($n$ = 1) **IIa–f** ($n$ = 2) **IIIa–f** ($n$ = 1) **Va–f** ($n$ = 2) **IVa–f** ($n$ = 1) **VIa–c** ($n$ = 2)

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**Table 1.** Yields and ratio of reaction products obtained by treating 1,3-cyclopentadiene with sulfenamides activated with phosphorus oxyhalides

| $POHlg_3$ | Sulfenamide, Ar | Index | Reaction time, h | Ratio of reaction products, % | | | Overall yield, % |
|---|---|---|---|---|---|---|---|
| | | | | **I** | **III** | **IV** | |
| $POBr_3$ | 4-$NO_2C_6H_4$ | a | 2 | 22 | 40 | 38 | 95 |
| | 2-$NO_2C_6H_4$ | b | 20 | 29 | 42 | 29 | 95 |
| | $C_6H_5$ | c | 2 | 28 | 36 | 36 | 95 |
| $POCl_3$ | 4-$NO_2C_6H_4$ | d | 2 | 100 | – | – | 80 |
| | | | After 120 h of storage | 63 | 18 | 18 | |
| | | | After submitting to chromatography | – | 75 | 25 | 18 |
| | 2-$NO_2C_6H_4$ | e | 3 | 100 | – | – | 40[a] |
| | | | After 120 h of storage | 62 | 38 | – | |
| | | | 24 | 76 | 16 | 8 | 80[a] |
| | | | After 170 h of storage | 50 | 42 | 8 | |
| | $C_6H_5$ | f | 3 | 21 | 46 | 33 | 50 |

[a] Unreacted sulfenamide remained in the reaction mixture.

**Table 2.** Yields and ratio of reaction products obtained by treating 1,3-cyclohexadiene with sulfenamides activated with phosphorus oxyhalides

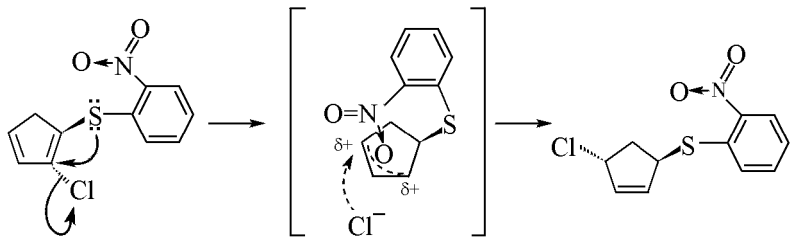
| $POHlg_3$ | Sulfenamide, Ar | Index | Reaction time, h | Ratio of reaction products, % | | | Overall yield, % |
|---|---|---|---|---|---|---|---|
| | | | | **II** | **V** | **VI** | |
| $POBr_3$ | 4-$NO_2C_6H_4$ | a | 3 | 50 | 50 | – | 80 |
| | | | After 120 h of storage | 18 | 66 | 16 | |
| | | | After boiling in $CHCl_3$ | 10 | 50 | 40 | 60 |
| | | | After submitting to chromatography | – | 77 | 23 | 30 |
| | 2-$NO_2C_6H_4$ | b | 18 | 25 | 75 | – | 85 |
| | | | 42 | 17 | 83 | – | 95 |
| | $C_6H_5$ | c | 1 | 23 | 56 | 21 | 78 |
| | | | After 120 h of storage | 25 | 50 | 25 | |
| $POCl_3$ | 4-$NO_2C_6H_4$ | d | 1.5 | 100 | – | – | 80[a] |
| | | | After 15O h of storage | 69 | 31 | – | |
| | | | 5 | 63 | 37 | – | 86 |
| | 2-$NO_2C_6H_4$ | e | 4 | 100 | – | – | 93[a] |
| | | | After 120 h of storage | 67 | 33 | – | |
| | | | 42 | 100 | – | – | 90[a] |
| | $C_6H_5$ | f | 4 | 66 | 34 | – | 60 |
| | | | After 120 h of storage | 40 | 60 | – | |

[a] Unreacted sulfenamide remained in the reaction mixture.

The data on yields and composition of reaction products obtained from 1,3-cyclopentadiene and 1,3-cyclohexadiene treated with the system arylsulfenamide–phosphorus oxyhalide are compiled in Tables 1 and 2 respectively.

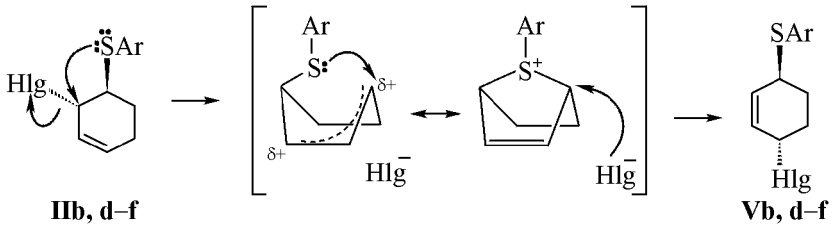
The isomerization of 4-arylsulfanyl-3-halocyclopent-1-enes (**Ia**–**f**) obtained by halosulfenylation of 1,3-cyclopentadiene resulted in a mixture of *trans*- and *cis*-isomers of 5-arylsulfanyl-3-halocyclopent-1-ene with significant prevalence of *trans*-isomer **III**. However in the case of 4-(*o*-nitrophenylsulfanyl)-3-chlorocyclopent-1-ene (**Ie**) was obtained almost sole isomerization product, *trans*-5-(o-nitrophenylsulfanyl)-3-chlorocyclopent-1-ene (**IIIe**), *cis*-isomer

**IVe** formed only in trace amount. Apparently the nitro group in the ortho position of benzene ring interacts with the arising carbocation and prevents the attack of the chloride ion from the *exo*-side.



**Ie** **IIIe**

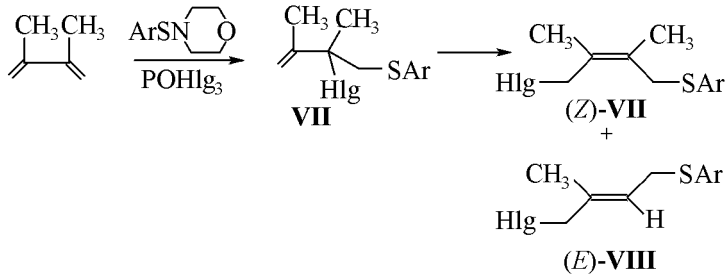
It should be noted that this effect is not observed with 3-bromo-4-(*o*-nitrophenylsulfanyl)cyclopen-1-ene (**Ib**). Apparently the attack on the carbocationic site of bromide anion which is a stronger nucleophile than chloride ion occurred faster than nitro group coordination. The data compiled in Table 2 show that isomerization of 4-arylsulfanyl-3-halocyclohex-1-enes (**IIb, d–f**) (1,3-cyclohexadiene adducts) afforded exclusively *trans*-5-arylsulfanyl-3-halocyclohex-1-enes (**Vb, d–f**). Probably here one unshared pair of sulfur atom can interact with a carbocation site arising in the fourth position of the cyclohexane ring.



**IIb, d–f** **Vb, d–f**

*cis*-Isomer **VI** was obtained only from 3-bromo-5-(*p*-nitrophenylsulfanyl)cyclohex-1-ene (**a**) and 3-bromo-5-phenylsulfanylcyclohex-1-ene (**c**). Same as with isomerization of cyclopentadiene adducts here assumption is possible of faster attack of bromide anion on the carbocation site as compared to the other nucleophiles (e.g., unshared electron pairs of sulfur).

The halosulfenylation of the symmetrical 2,3-dimethyl-1,3-butadiene similarly to reaction with cyclic dienes afforded a single 1,2-adduct that isomerized



**VII**

(*Z*)-**VII** + (*E*)-**VIII**

into *E*- and *Z*-isomers of 4-arylsulfanyl-1-halo-2,3-dimethyl-1-butene.

The yields and ratio of reaction products obtained from 2,3-dimethyl-1,3-butadiene and arylsulfenamides activated with phosphorus oxyhalides are listed in Table 3.

With unsymmetrical 1,3-diene, isoprene, the situation is far more complicated since are presumable two

**Table 3.** Yields and ratio of reaction products obtained by treating 2,3-dimethyl-1,3-butadiene with sulfenamides activated with phosphorus oxyhalides

| $POHlg_3$ | Sulfenamide, Ar | Index | Reaction time, h | Ratio of reaction products, % | | | Overall yield, % |
|---|---|---|---|---|---|---|---|
| | | | | **VII** | **(*E*)-VIII** | **(*Z*)-VIII** | |
| $POBr_3$ | 4-$NO_2C_6H_4$ | a | 2 | 10 | 40 | 40 | 57 |
| | 2-$NO_2C_6H_4$ | b | 17 | – | 40 | 60 | 90 |
| | $C_6H_5$ | c | 2 | – | 50 | 50 | 87 |
| $POCl_3$ | 4-$NO_2C_6H_4$ | d | 27 | 74 | 7 | 19 | 85 |
| | 2-$NO_2C_6H_4$ | e | 17 | 58 | 14 | 28 | 59[a] |
| | | | 21 | 40 | 20 | 40 | 32[a] |
| | $C_6H_5$ | f | 3 | 82 | 9 | 9 | 75 |

[a] Unreacted sulfenamide remained in the reaction mixture.

**Table 4.** Yields and ratio of reaction products obtained by treating isoprene with sulfenamides activated with phosphorus oxyhalides

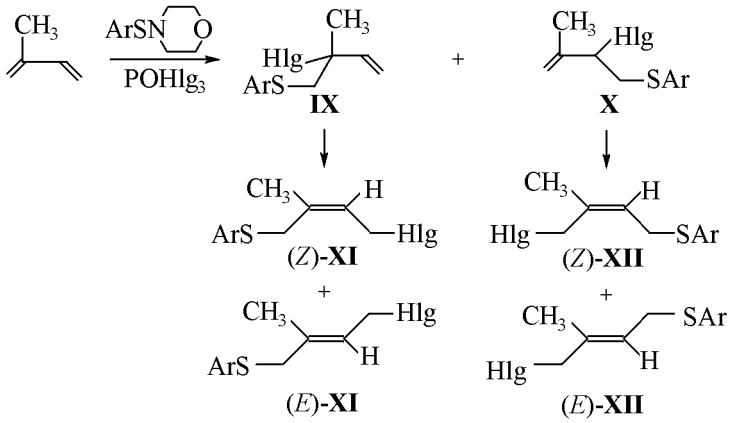
| $POHlg_3$ | Sulfenamide, Ar | Index | Reaction time, h | Ratio of reaction products, % | | | | | Overall yield, % |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **IX** | **X** | **(*Z*)-XI** | **(*E*)-XI** | **(*E*)-XI** | |
| $POBr_3$ | 4-$NO_2C_6H_4$ | a | 2 | – | 10 | 60 | 30 | – | 96 |
| | 2-$NO_2C_6H_4$ | b | 18 | 21 | 15 | 48 | 16 | – | 90 |
| | $C_6H_5$ | c | 2 | – | 11 | 53 | 20 | 16 | 77 |
| POCl3 | 4-$NO_2C_6H_4$ | d | 27 | 50 | 23 | 27 | – | – | 95 |
| | 2-$NO_2C_6H_4$ | e | 27 | 33 | 20 | 34 | 13 | – | 51[a] |
| | $C_6H_5$ | f | 2 | 9 | 23 | 38 | 38 | – | 89 |

[a] Unreacted sulfenamide remained in the reaction mixture.

1,2-adducts arising in keeping with Markownikoff rule, and 4 isomers of 1,4-adduct (see Table 4).

It is clear, that *E*- and *Z*-isomers of compound **XI** arise as a result of adduct **IX** isomerization, and isomerization of adduct **X** can furnish (*Z*)-(**XII**) and (*E*)-(**XII**) of which only isomer (*E*)-(**XII**) is obtained.

The data in Table 4 show that arenesulfenamides activated with phosphorus oxyhalides react predominantly with the more substituted double bond of



the isoprene. As a result forms compound **IX**, and its isomerization gives rise to isomers (*Z*)-(**XI**) and (*E*)-(**XI**). Product **X** originating from the reaction at the less substituted isoprene double bond forms in considerably smaller amount and almost does not suffer isomerization.

We revealed certain laws governing reactions with all dienes studied. The rate of reaction with dienes of sulfenamides activated with $POHlg_3$ depends not only on the proper structure of the diene but also on the character of the halogen and of substituents in the benzene ring of the sulfenamide. The cyclic dienes react with the sulfenamides activated with phosphorus oxyhalides faster, than open-chain analogs (2,3-dimethyl-1,3-butadiene and isoprene). The reaction of *N*-(*o*-nitriphenylsulfanyl)morpholine activated with $POHlg_3$ (Hlg = Cl, Br) with dienes is about 10 times slower than reactions of *N*-(*p*-nitrophenyl)- and *N*-phenylsulfanylmorpholine.

Sulfenamides react faster in the presence of $POBr_3$ than $POCl_3$ resulting in higher yilds of bromosulfides as compared to chlorosulfides. Besides 1,2-adducts of bromosulfenylation easier undergo isomerization into 1,4-adducts that the chlorosulfides because bromide anion is a better leaving group than chloride anion, and the primarily formed bromosulfides easier transform into the corresponding carbocations than the respective chlorosulfides.

It should be noted that isomerization of products obtained by bromo- and chlorosulfenylation by *N*-phenylsulfanylmorpholine occurs faster than the isomerization of halosulfenylation products prepared with the use of nitro-substituted arylsulfenamides. Apparently the PhS group as a better donor than $O_2NC_6H_4S$ group provides better stabilization of the arising carbocation and thus facilitates the isomerization.

The structure of products obtained was deduced from the 1H NMR spectra. The analysis of spectra and their subsequent description were based on the published data, on the values of the $^1H$–$^1H$ coupling constants, and also on the results of homonuclear double resonance spectra. The chemical shifts of protons and coupling constants in the $^1H$ NMR spectra of compounds synthesized are compiled in Tables 5–15.

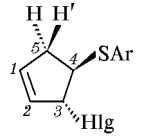
Configuration assignments of compounds **I, III, IV** were based on analysis of coupling constants $^3J$ values and on analogous published data [7–11]. Note that conformational mobility of substituted cyclopentenes is insignificant, and prevails the *envelope* conformation where $C^4$ atom is outside the plane formed by the other four carbon atoms [9]. This fact significantly simplifies the interpretation of coupling constants in the course of structural assignment.

In the 1H NMR spectra of compounds **I** (Table 5) the signals of protons at the double bond appear as two multiplets, and methylene protons have quite different chemical shifts (3.30–3.15 and 2.50–2.40 ppm) and forms (doublet of doublets of quartets and doublet of doublets of triplets respectively). By an example of compound **Ie** it was established applying the homonuclear double resonance procedure that the coupling constant of olefin protons is 5.8 Hz, and the constants of their coupling with the protons of $CH_2$ group are 1.5–2.0 Hz. The proton signals of substituents in compounds **I** look as follows: H–CHlg is a broadened singlet or a triplet with a coupling constant of about 2.0 Hz , H–CS is a doublet with a coupling constant of ~7.0 Hz. According to published data [9] substituted cyclopentenes have the values of $^3J_{trans}$ 3.0–4.0 and $^3J_{cis}$ 6.0–8.0 Hz. The lack of large coupling constant by H–CHlg atom and a common large coupling constant by H–CS and by one of the protons of the $CH_2$ group (7.0 Hz) allow assignment to compounds **I** a structure of 1,2-*trans*-adduct of 1,3-cyclopentadiene.

The structure of 1,4-adducts was assigned to products **III** and **IV** by analogy with the published data [7, 8, 11]. The signals from olefin protons of compounds **III** and **IV** appear as a sole multiplet. The signals from the other four protons of compounds **III** and **IV** (H–CHlg, H–CS and $CH_2$) are dissimilar in form and chemical shifts (Tables 6 and 7). As already mentioned, the coupling constants in the spectra of substituted cyclopentenes have values $^3J_{trans}$ 3.0–4.0 and $^3J_{cis}$ 6.0–8.0 Hz [9]. The comparison of these values with the sets of coupling constants of isomers **III** and **IV** given in tables shows that the protons $H^4$ and $H^{4'}$ in compound **III** are in different configurational relations to protons $H^3$ and $H^5$, whereas in the isomer **IV** the protons $H^3$ and $H^5$ are configurationally equivalent with respect to protons $H^4$ and $H^{4'}$. Consequently compounds **III** are *trans*-isomers, and compounds **IV** *cis*-isomers of 5-arylsulfanyl-3-halocyclopent-1-enes.

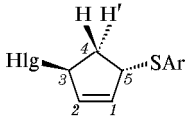
The structure of compounds **IId** and **Va** (Table 8) was established applying the method of homonuclear $^1H$–$^1H$ double resonance. It was shown that the proton H–CS in compound **IId** is coupled with the proton H–CCl and the protons of the adjacent $CH_2$ group whereas the H–CCl is coupled with H–CS and with one of the olefin protons. These data un-

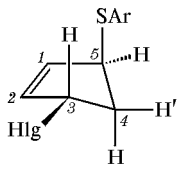
**Table 5.** Chemical shifts of $^{1}$H nuclei (δ, ppm ) and coupling constants $^{1}$H–$^{1}$H (*J* Hz) of compounds **Ia–f**

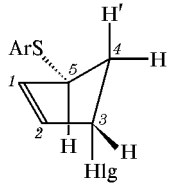



| Compd. no. | $H^{1}$ | $H^{2}$ | $H^{3}$ | $H^{4}$ | $H^{5}$ | $H^{5'}$ | H(Ar) |
|---|---|---|---|---|---|---|---|
| **Ia** | 6.19–5.97 m | | 4.92 t ($J_{3,4}$ = $J_{3,5}$ = 1.9) | 4.34 m ($J_{4,5}$ 7.0) $J_{5,4}$ 7.0, $J_{5,1}$ = $J_{5,2}$ = $J_{5,3}$ = 1.9) | 3.28 d.d.q ($^{2}J_{5,5'}$ 18.5, $J_{5',4}$ 3.0, $J_{5',1}$ = $J_{5',2}$ = 1.5) | 2.43 d.d.t ($2J_{5',5}$ 18.5, | 8.16 d (*J* 9.1); 7.41 d (*J* 9.1) |
| **Ib** | 6.20–5.95 m | | 4.90 t ($J_{3,4}$ = $J_{3,5}$ = 2.0) | 4.29 m ($J_{4,5}$ 7.1) $J_{5,4}$ 7.1, $J_{5,1}$ = $J_{5,2}$ = $J_{5,3}$ = 2.0) | 3.30 d.d.q ($2J_{5,5'}$ 18.6, $J_{5',4}$ 2.9, $J_{5',1}$ = $J_{5',2}$ = 1.4) | 2.50 d.d.t ($2J_{5',5}$ 18.6, | 8.22–7.28 m |
| **Ic** | 6.04–5.94 m | | 4.95 br.s | 4.23 d ($J_{4,5}$ = 6.9) $J_{5,4}$ 6.9, $J_{5,1}$ = $J_{5,2}$ = $J_{5,3}$ = 2.0) | 3.15 d.d.d ($2J_{5,5'}$ 18.1, | 2.40 m | 7.50–7.00 m |
| **Id** | 5.89 m ($J_{1,2}$ 5.8, $J_{1,5}$ = $J_{1,5'}$ = 2.0) | 6.07 m ($J_{2,1}$ 5.8, $J_{2,5}$ = $J_{2,5'}$ = 2.0) | 4.85 br.s | 4.19 d ($J_{4,5}$ 7.3) | 3.28 d.d.d ($2J_{5,5'}$ 18.4, $J_{5,4}$ 7.3, $J_{5,1}$ = $J_{5,2}$ = $J_{5,3}$ = 2.0) | 2.44 d.d.t ($2J_{5',5}$ 18.4, $J_{5',4}$ 2.4, $J_{5',1}$ = $J_{5',2}$ = 2.0) | 8.16 d (*J* 9.1); 7.41 d (*J* 9.1) |
| **Id** | 5.88 m ($J_{1,2}$ 5.7, $J_{1,5}$ = $J_{1,5'}$ = 2.1) | 6.08 m ($J_{2,1}$ 5.7, $J_{2,5}$ = $J_{2,5}$ = 2.1) | 4.84 br.s | 4.15 d ($J_{4,5}$ 7.4) | 3.30 d.d.d ($2J_{5,5'}$ 18.5, $J_{5,4}$ 7.4, $J_{5,1}$ = $J_{5,2}$ = $J_{5,3}$ = 2.1) | 2.51 d.d.t ($2J_{5',5}$ 18.5, $J_{5',4}$ 2.7, $J_{5',1}$ = $J_{5',2}$ = 2.1) | 8.22–7.28 m |
| **If** | 5.83 m | 5.99 m | 4.85 br.s | 4.05 d.t ($J_{4,5}$ 7.2, $J_{4,5}$ = J4,3 = 2.0) | 3.12 d.d.d ($2J_{5,5'}$ 18.1, $J_{5,4}$ 7.2, $J_{5,1}$ = $J_{5,2}$ = $J_{5,3}$ = 2.1) | 2.51 d.d ($2J_{5',5}$ 18.1, $J_{5',1}$ = $J_{5',2}$ = $J_{5',4}$ = 2.0) | 7.60–7.10 m |

**Table 6.** Chemical shifts of $^{1}$H nuclei (δ, ppm ) and coupling constants $^{1}$H–$^{1}$H (*J* Hz) of compounds **IIIa–f**

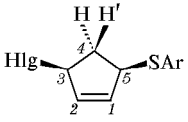


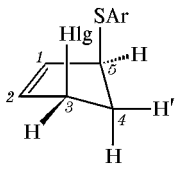



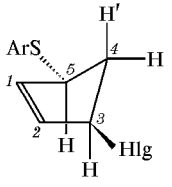




| Compd. no. | $H^{1}$ | $H^{2}$ | $H^{3}$ | $H^{4}$ | $H^{4'}$ | $H^{5}$ | H(Ar) |
|---|---|---|---|---|---|---|---|
| **IIIa** | 6.19–5.97 m | 5.10 d.d ($J_{3,4'}$ 7.1, $J_{3,4}$ = $J_{3,2}$ = $J_{3,1}$ = 2.2) | 2.94 d.d.q (2$J_{4,4'}$ 15.2, $J_{4,5}$ 7.1, $J_{4,3}$ 2.2) | 2.53 d.d.d ($^{2}J_{4',4}$ 15.2, $J_{4',3}$ 7.1, $J_{4',5}$ 5.8) | 4.65 m | 8.14 d (*J* 9.1); 7.40 d (*J* 9.1) |
| **IIIb** | 6.20–5.96 m | 5.15 d.d ($J_{3,4'}$ 7.1, $J_{3,4}$ = $J_{3,1}$ = $J_{3,2}$ = 2.3) | 2.96 d.d.q (2$J_{4,4'}$ 15.2, $J_{4,5}$ 7.1, $J_{4,3}$ 2.3) | 2.58 d.d.d ($^{2}J_{4',4}$ 15.2, $J_{4',3}$ 7.1, $J_{4',5}$ 5.8) | 4.64 m | 8.22–7.28 m |
| **IIIc** | 6.04–5.94 m | 4.97 d.d ($J_{3,4'}$ 7.4, $J_{3,4}$ = $J_{3,2}$ = $J_{3,1}$ = 2.2) | 2.81 d.d.q (2$J_{4,4'}$ 15.2, $J_{4,5}$ 7.2, $J_{4,3}$ 2.2) | 2.48 d.d.d ($^{2}J_{4',4}$ 15.2, $J_{4',3}$ 7.4, $J_{4',5}$ 5.0) | 4.43 m | 7.50–7.20 m |
| **IIId** | 6.09–6.02 m | 5.05 d.d ($J_{3,4'}$ 7.0, $J_{3,4}$ = $J_{3,1}$ = $J_{3,2}$ = 2.3) | 2.75 d.d.q (2$J_{4,4'}$ 14.8, $J_{4,5}$ 7.0, $J_{4,3}$ 2.3) | 2.50 d.d.d ($^{2}J_{4',4}$ 14.8, $J_{4',3}$ 7.0, $J_{4',5}$ 4.8) | 4.65 m | 8.12 d (*J* 9.1); 7.40 d (*J* 9.1) |
| **IIId** | 6.11–6.04 m | 5.10 d.d ($J_{3,4'}$ 7.3, $J_{3,4}$ = $J_{3,1}$ = $J_{3,2}$ = 2.5) | 2.78 d.d.q (2$J_{4,4'}$ 15.0, $J_{4,5}$ 7.4, $J_{4,3}$ 2.5) | 2.54 d.d.d ($^{2}J_{4',4}$ 15.0, $J_{4',3}$ 7.3, $J_{4',5}$ 5.1) | 4.64 m | 8.22–7.28 m |
| **IIIf** | 5.99–5.87 m | 4.90 m ($J_{3,4'}$ 7.2) | 2.60 d.d.d (2$J_{4,4'}$ 14.9, $J_{4,5}$ 7.5, $J_{4,3}$ 3.2) | 2.44 d.d.d ($^{2}J_{4',4}$ 14.9, $J_{4',3}$ 7.2, $J_{4',5}$ 5.0) | 4.40 m | 7.60–7.10 m |

**Table 7.** Chemical shifts of $^{1}$H nuclei (δ, ppm ) and coupling constants $^{1}$H–$^{1}$H (*J* Hz) of compounds **IVa–f**

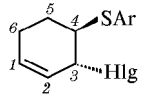


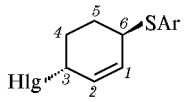

| Compd. no. | $H^{1}$ | $H^{2}$ | $H^{3}$ | $H^{4}$ | $H^{4'}$ | $H^{5}$ | H(Ar) |
|---|---|---|---|---|---|---|---|
| **IVa** | 6.19–5.97 m | 5.06 d.t ($J_{3,4}$ 7.6, $J_{3,4}$ = $J_{3,2}$ = 2.0) | 3.14 d.t (2$J_{4,4'}$ 15.5, $J_{4,3}$ = $J_{4,5}$ = 7.6) | 2.52 d.t ($^{2}J_{4',4}$ 15.5, $J_{4',3}$ = $J_{4',5}$ = 2.0) | 4.52 m ($J_{5,4}$ 7.6) 7.39 d (*J* 9.1) | 8.16 d (*J* 9.1); |
| **IVb** | 6.20–5.96 m | 5.08 d.t ($J_{3,4}$ 7.6, $J_{3,4}$ = $J_{3,2}$ = 2.2) | 3.18 d.t (2$J_{4,4'}$ 15.5, $J_{4,3}$ = $J_{4,5}$ = 7.6) | 2.55 d.t ($^{2}J_{4',4}$ 15.5, $J_{4',3}$ = $J_{4',5}$ = 2.2) | 4.49 m ($J_{5,4}$ 7.6) | 8.22–7.28 m |
| **IVc** | 6.04–5.94 m | 5.01 d.t ($J_{3,4}$ 7.7, $J_{3,4}$ = $J_{3,2}$ = 2.4) | 3.01 d.t (2$J_{4,4'}$ 15.5, $J_{4,3}$ = $J_{4,5}$ = 7.7) | 2.48 d.t ($^{2}J_{4',4}$ 15.5, $J_{4',3}$ = $J_{4',5}$ = 2.4) | 4.31 m ($J_{5,4}$ 7.7) | 7.50–7.20 m |
| **IVd** | 6.09–6.02 m | 4.99 d.t ($J_{3,4}$ 7.7, $J_{3,4}$ = $J_{3,2}$ = 2.6) | 3.10 d.t (2$J_{4,4'}$ 15.4, $J_{4,3}$ = $J_{4,5}$ =7.7) | 2.33 d.t ($^{2}J_{4',4}$ 15.4, $J_{4',3}$ = $J_{4',5}$ = 2.6) | 4.43 m ($J_{5,4}$ 7.7) | 8.14 d (*J* 9.1); 7.41 d (*J* 9.1) |
| **IVd** | 6.11–6.04 m | 5.01 d ($J_{3,4}$ 7.7) | 3.12 d.t (2$J_{4,4'}$ 15.4, $J_{4,3}$ = $J_{4,5}$ = 7.7) | 2.36 d.t ($^{2}J_{4',4}$ 15.4, $J_{4',3}$ = $J_{4',5}$ = 2.5) | 4.39 m ($J_{5,4}$ 7.7) | 8.22–7.28 m |
| **IVf** | 5.99–5.87 m | 4.86 m ($J_{3,4}$ 7.6) | 2.95 d.t ($J_{4,4'}$ 15.5, $J_{4,3}$ = $J_{4,5}$ = 7.6) | 2.25 d.t ($^{2}J_{4',4}$ 15.5, $J_{4',3}$ = $J_{4',5}$ = 3.2) | 4.19 m | 7.60–7.10 m |

**Table 8.** Chemical shifts of $^1$H nuclei (δ, ppm ) and coupling constants $^1$H–$^1$H (*J* Hz) of compounds **IIa–f**



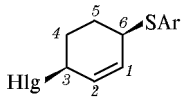

| Compd. no. | $H^1$ | $H^2$ | $H^3$ | $H^4$ | $H_2C^5$; $H_2C^6$ | H(Ar) |
|---|---|---|---|---|---|---|
| **IIa** | 5.91 m ($J_{1,2}$ 10.0, $J_{1,6}$ 4.7, $J_{1,6}$ 2.3) | 5.85 m | 4.70 m | 4.08 m ($J_{4,5}$ 5.9, $J_{4,3}$ = $J_{4,5}$ = 2.8) | 2.60–1.85 m | 8.14 d (*J* 9.0); 7.39 d (*J* 9.0) |
| **IIb** | 5.90 m | 5.87 m | 4.72 m | 4.05 m | 2.50–1.88 m | 8.12 d (*J* 8.2); 7.62 d (*J* 8.2); 7.48 t (*J* 8.2); 7.32 t (*J* 8.2) |
| **IIc** | 5.82 m | 5.71 m | 4.70 m | 3.86 m | 2.45–1.76 m | 7.50–7.16 m |
| **IId** | 5.96 m ($J_{1,2}$ 10.0, $J_{1,6}$ 4.4, $J_{1,6'}$ 3.3) | 5.78 m ($J_{2,1}$10.0, $J_{2,3}$ 4.6, $J_{2,6}$ = $J_{2,6'}$ = 2.2) | 4.51 m ($J_{3,2}$ 4.6, $J_{3,4}$ 3.3) | 3.92 m ($J_{4,5}$ 4.7, $J_{4,3}$ = $J_{4,5}$ = 3.3) | 2.43 m, 2.30 m, 2.21 m, 1.95 m | 8.15 d (*J* 9.1); 7.40 d (*J* 9.1) |
| **IIe** | 5.95 m ($J_{1,2}$ 9.9, $J_{1,6}$ 4.9, $J_{1,6}$ 2.9) | 5.77 m ($J_{2,1}$ 9.9) | 4.53 m ($J_{3,2}$ 4.6, $J_{3,4}$ 3.2) | 3.90 m ($J_{4,5}$ 4.6, $J_{4,3}$ = $J_{4,5}$ = 3.2) | 2.42 m, 2.37 m, 2.20 m, 2.20 m | 8.10 d (*J* 8.7); 7.60 d (*J* 8.7); 7.50 t (*J* 8.7); 7.30 t (*J* 8.7) |
| **IIf** | 5.90 m ($J_{1,2}$ 10.0) | 5.76 m ($J_{2,1}$ 10.0) | 4.48 m ($J_{3,2}$ 4.8, $J_{3,4}$ 3.4) | 3.68 m ($J_{4,5}$ 4.9, $J_{4,3}$ = $J_{4,5}$ = 3.4) | 2.43–1.60 m | 7.50–7.15 m |

**Table 9.** Chemical shifts of $^1$H nuclei (δ, ppm ) and coupling constants $^1$H–$^1$H (*J* Hz) of compounds **Va–f**



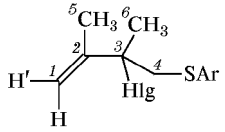

| Compd. no. | $H^1$ | $H^2$ | $H^3$ | $H^6$ | $H_2C^4$; $H_2C^5$ | H(Ar) |
|---|---|---|---|---|---|---|
| Va | 6.10 d.d.t ($J_{1,2}$ 9.7, $J_{1,6}$ 4.7, J = 1.2, 1.2) | 5.85 d.d.t ($J_{2,1}$ 9.7, $J_{2,3}$ 4.9, J = 1.0, 1.0) | 4.80 m | 4.22 m | 2.60–1.85 m | 8.12 d (*J* 8.7); 7.38 d (*J* 8.7) |
| Vb | 6.12 d.d.t ($J_{1,2}$ 9.6, $J_{1,6}$ 4.7, J = 1.2, 1.2) | 5.86 d.d.t ($J_{2,1}$ 9.6, $J_{2,3}$ 4.7, J = 1.1, 1.1) | 4.81 m | 4.20 m | 2.50–1.88 m | 8.11 d (*J* 8.3); 7.58 d (*J* 8.3); 7.52 t (*J* 8.3); 7.29 t (*J* 8.3) |
| Vc | 5.98 d.d.t ($J_{1,2}$ 9.5, $J_{1,6}$ 4.7, J = 1.3, 1.3) | 5.85 d.d.t ($J_{2,1}$ 9.6, $J_{2,3}$ 4.8, J = 1.1, 1.1) | 4.75 m | 3.92 m | 2.45–1.76 m | 7.50–7.16 m |
| Vd | 6.02 d.d.t ($J_{1,2}$ 10.0, $J_{1,6}$ 4.8, J = 1.1, 1.1) | 5.91 d.d.t ($J_{2,1}$ 10.0, $J_{2,3}$ 4.8, J = 1.2, 1.2) | 4.60 m | 4.15 m | 2.48–1.84 m | 8.17 d (*J* 9.1); 7.39 d (*J* 9.1) |
| Vd | 6.01 m ($J_{1,2}$ 9.8, $J_{1,6}$ 4.7) | 5.91 m ($J_{2,1}$ 9.8, $J_{2,3}$ 4.5) | 4.60 m | 4.13 m | 2.50–1.98 m | 8.22–7.28 m |
| Vf | 5.91 m | 5.85 m | 4.56 m | 3.86 m | 2.50–1.70 m | 7.60–7.20 m |

**Table 10.** Chemical shifts of $^{1}$H nuclei (δ, ppm ) and coupling constants $^{1}$H–$^{1}$H (*J*, Hz) of compounds **VI–f**




| Compd. no. | $H^1$ | $H^2$ | $H^3$ | $H^6$ | $H_2C^4$; $H_2C^5$ | H(Ar) |
|---|---|---|---|---|---|---|
| **VIa** | 6.06 d.d.d.d ($J_{1,2}$ 10.0, $J_{1,6}$ 4.4, *J* 2.2, *J* 1.0) | 5.80 d.d.d ($J_{2,1}$ 10.0, $J_{2,3}$ 2.8) | 4.77 m | 4.10 m | 2.60–1.85 m | 8.12 d (*J* 8.7); 7.38 d (*J* 8.7) |
| **VIc** | 5.92 d.d.d.d ($J_{1,2}$ 10.0, $J_{1,6}$ 4.4, *J* 2.2, *J* 1.2) | 5.78 d.d.t ($J_{2,1}$ 10.0, $J_{2,3}$ 2.9, *J* = 0.9, 0.9) | 4.68 m | 3.80 m | 2.45–1.76 m | 7.50–7.16 m |

**Table 11.** Chemical shifts of $^{1}$H nuclei (δ, ppm ) and coupling constants $^{1}$H–$^{1}$H ((25)J, Hz) of compounds **VII–f**




| Compd. no. | $H^1$ | $H^{1'}$ | $H^4$ | $H_3C^5$ | $H_3C^6$ | H(Ar) |
|---|---|---|---|---|---|---|
| **VIIa** | 5.20 s | 5.08 q ($J_{1',5}$ 1.3) | 3.60 d ($2J_{4,4'}$ 13.3); 3.43 d ($2J_{4,4'}$ 13.3) | 1.96–1.83 m | | 8.10 d (*J* 8.8); 7.36 d (*J* 8.8) |
| **VIId** | 5.15 s | 5.03 q ($J_{1',5}$ 1.4) | 3.62 d ($2J_{4,4'}$ 12.6); 3.54 d ($2J_{4,4'}$ 12.6) | 1.89 d ($J_{5,1}$ 1.4) | 1.85 s | 8.09 d (*J* 9.0); 7.39 d (*J* 9.0) |
| **VIId** | 5.17 s | 5.04 q ($J_{1',5}$ 1.5) | 3.59 d ($2J_{4,4'}$ 11.8); 3.45 d ($2J_{4,4'}$ 11.8) | 1.96–1.83 m | | 8.32–7.20 m |
| **VIIf** | 5.09 s | 4.87 q ($J_{1',5}$ 1.4) | 3.59 d ($2J_{4,4'}$ 13.0); 3.45 d ($2J_{4,4'}$ 13.0) | 1.73 d ($J_{5,1}$ 1.4) | 1.37 s | 7.51–7.12 m |

**Table 12.** Chemical shifts of $^1$H nuclei (δ, ppm ) and coupling constants $^1$H–$^1$H (*J* Hz) of compounds **VIIIa**–**f**

| Compd. no. | Isomer | $H^1$ | $H^4$ | $H_3C^5$ | $H_3C^6$ | H(Ar) |
|---|---|---|---|---|---|---|
| **VIIIa** | *E* | 4.02 s | 3.76 s | 1.86 s | 1.85 s | 8.12 d (*J* 8.8); 7.36 d (*J* 8.8) |
| | *Z* | 4.00 s | 3.69 s | 1.89 q (*J* 1.5) | 1.83 q (*J* 1.5) | 8.10 d (*J* 8.8); 7.36 d (*J* 8.8) |
| **VIIIb** | *E* | 4.04 s | 3.68 s | 1.90–1.83 m | | 8.18–7.24 m |
| | *Z* | 4.01 s | 3.62 s | 1.90–1.83 m | | 8.14–7.24 m |
| **VIIIc** | *E* | 3.94 s | 3.57 s | 1.82 q (*J* 0.9) | 1.76 q (*J* 0.9) | 7.37–7.17 m |
| | *Z* | 3.75 s | 3.50 s | 1.86 q (*J* 1.3) | 1.56 q (*J* 1.4) | 7.37–7.17 m |
| **VIIId** | *E* | 4.08 s | 3.75 s | 1.91–1.79 m | | 8.09 d (*J* 9.2); 7.40 d (*J* 9.2) |
| | *Z* | 4.07 s | 3.68 s | 1.91–1.79 m | | 8.07 d (*J* 9.0); 7.33 d (*J* 9.0) |
| **VIIIe** | *E* | 4.11 s | 3.68 s | 1.96–1.83 m | | 8.32–7.20 m |
| | *Z* | 4.09 s | 3.63 s | 1.96–1.83 m | | 8.32–7.20 m |
| **VIIIf** | *E* | 4.02 s | 3.56 s | 1.83 s | 1.74 s | 7.51–7.12 m |
| | *Z* | 3.79 s | 3.51 s | 1.88 q (*J* 1.4) | 1.56 q (*J* 1.4) | 7.51–7.12 m |

**Table 13.** Chemical shifts of $^1$H nuclei (δ, ppm ) and coupling constants $^1$H–$^1$H (*J* Hz) of compounds **IXb, d**–**e**

| Compd. no. | $H^{1'}$ | $H^1$ | $H^2$ | $H_2C^4$ | $H_3C^5$ | H(Ar) |
|---|---|---|---|---|---|---|
| **IXb** | 5.14 d ($J_{1,2}$ 10.7) | 5.35 d ($J_{1,2}$ 17.3) | 5.97 d.d ($J_{2,1}$ 17.3, $J_{2,1}$ 10.7) | 3.22 d, 3.14 d ($2J_{4,4}$ 12.3) | 1.85 s | 8.19–7.21 m |
| **IXd** | 5.19 d ($J_{1,2}$ 10.7) | 5.37 d ($J_{1,2}$ 17.0) | 6.03 d.d ($J_{2,1}$ 17.0, $J_{2,1}$ 10.7) | 3.26 d, 3.19 d ($2J_{4,4}$ 13.2) | 1.78 s | 8.20–8.03 m, 7.41–7.29 m |
| **IXd** | 5.19 d ($J_{1,2}$ 10.6) | 5.38 d ($J_{1,2}$ 17.2) | 6.04 d.d ($J_{2,1}$ 17.2, $J_{2,1}$ 10.6) | 3.25 d, 3.17 d ($2J_{4,4}$ 12.5) | 1.83 s | 8.34–7.24 m |
| **IXf** | 5.13 d ($J_{1,2}$ 10.7) | 5.31 d ($J_{1,2}$ 17.2) | 5.99 d.d ($J_{2,1}$ 17.2, $J_{2,1}$ 10.7) | 3.19 d, 3.08 d ($2J_{4,4}$ 13.3) | 1.76 s | 7.40–7.12 m |

**Table 14.** Chemical shifts of $^1$H nuclei (δ, ppm ) and coupling constants $^1$H–$^1$H (*J* Hz) of compounds **Xa**–**f**

| Compd. no. | $H^1$ | $H^{1'}$ | $H^3$ | $H_2C^4$ | $H_3C^5$ | H(Ar) |
|---|---|---|---|---|---|---|
| **Xa** | 5.00 br.s | 5.08 br.s | 4.65 d.d ($J_{3,4'}$ 9.9, $J_{3,4}$ 5.7) | 3.63 d.d ($2J_{4,4'}$ 13.0, $J_{4,3}$ 5.7), 3.50 d.d ($2J_{4,4'}$ 13.0, $J_{4',3}$ 9.9) | 1.83 s | 8.16–8.04 m, 7.38–7.30 m |
| **Xb** | 4.98 t ($J_{1,1}$ 1.2) | 5.08 br.s | 4.70 d.d ($J_{3,4'}$ 10.1, $J_{3,4}$ 5.5) | 3.59 d.d ($2J_{4,4'}$ 13.3, $J_{4,3}$ 5.5), 3.45 d.d ($2J_{4,4'}$ 13.3, $J_{4',3}$ 10.1) | 1.85 s | 8.19–7.21 m |
| **Xc** | 5.00 t ($J_{1,1}$ 1.4) | 5.08 br.s | 4.61 d.d ($J_{3,4'}$ 10.4, $J_{3,4}$ 5.4) | 3.52 d.d ($2J_{4,4'}$ 13.7, $J_{4,3}$ 5.4), 3.36 d.d ($2J_{4,4'}$ 13.7, $J_{4',3}$ 10.4) | 1.82 s | 7.40–7.12 m |
| **Xd** | 5.01 t ($J_{1,1}$ 1.2) | 5.05 br.s | 4.52 d.d ($J_{3,4'}$ 8.6, $J_{3,4}$ 6.5) | 3.50 d.d ($2J_{4,4'}$ 13.5, $J_{4,3}$ 6.5), 3.38 d.d ($2J_{4,4'}$ 13.5, $J_{4',3}$ 8.6) | 1.82 s | 8.20–8.03 m, 7.41–7.29 m |
| **Xe** | 5.00 t ($J_{1,1}$ 1.2) | 5.04 br.s | 4.57 d.d ($J_{3,4'}$ 8.8, $J_{3,4}$ 6.2) | 3.46 d.d ($2J_{4,4'}$ 13.2, $J_{4,3}$ 6.2), 3.34 d.d ($2J_{4,4'}$ 13.2, $J_{4',3}$ 8.8) | 1.83 s | 8.34–7.24 m |
| **Xf** | 4.97 t ($J_{1,1}$ 1.3) | 5.00 br.s | 4.43 d.d ($J_{3,4'}$ 9.2, $J_{3,4}$ 6.0) | 3.35 d.d ($2J_{4,4'}$ 13.8, $J_{4,3}$ 6.0), 3.22 d.d ($2J_{4,4'}$ 13.8, $J_{4',3}$ 9.2) | 1.87 s | 7.40–7.12 m |

ambiguously indicate the structure of 1,2-adduct. In the case of compound **Va** both protons H–CS and H–CBr are coupled with the protons at the double bond with a constant equal to 4.7–4.9 Hz (Table 9) evidencing the structure of 1,4-adduct.

*trans*-Location of substituents in compounds **IId** and **Vd** was proved applying ω-criterion. The essence of the method consists in measuring half-width of signals from protons attached to the substituents in the $^1$H NMR spectra registered in solvents

**Table 15.** Chemical shifts of $^1$H nuclei (δ, ppm ) and coupling constants $^1$H–$^1$H (*J*, Hz) of compounds **XIa–f, XIIc**

| Compd. no. | Isomer | H–C = | $H_2CHlg$ | $H_2CS$ | $CH_3$ | H(Ar) |
|---|---|---|---|---|---|---|
| **XIa** | *Z* | 5.77 t.q (*J* 8.4, *J* 1.2) | 3.93 d (*J* 8.4) | 3.64 s | 1.83 br.s | 8.16–8.04 m, 7.38–7.30 m |
| | *E* | 5.73 t (*J* 8.2) | 3.95 d (*J* 8.2) | 3.73 s | 1.90 br.s | 8.16–8.04 m, 7.38–7.30 m |
| **XIb** | *Z* | 5.83 t.q (*J* 8.4, *J* 1.2) | 3.96 d (*J* 8.4) | 3.62 s | 1.86 d (*J* 1.2) | 8.19–7.21 m |
| | *E* | 5.87 t (*J* 8.8) | 4.00 d (*J* 8.8) | 3.68 s | 1.93 br.s | 8.19–7.21 m |
| **XIc** | *Z* | 5.54 t.q (*J* 8.3, *J* 1.2) | 3.91 d (*J* 8.3) | 3.48 s | 1.85 d (*J* 1.2) | 7.40–7.12 m |
| | *E* | 5.60 t (*J* 8.4) | 3.95 d (*J* 8.4) | 3.56 s | 1.82 br.s | 7.40–7.12 m |
| **XId** | *Z* | 5.70 t.q (*J* 8.0, *J* 1.3) | 4.04 d (*J* 8.0) | 3.64 s | 1.82 d (*J* 1.3) | 8.20–8.03 m, 7.41–7.29 m |
| **XIe** | *Z* | 5.75 t.q (*J* 8.0, *J* 1.2) | 4.06 d (*J* 8.0) | 3.61 s | 1.86 d (*J* 1.2) | 8.34–7.24 m |
| | E | 5.70 t (*J* 8.6) | 4.09 d (*J* 8.6) | 3.68 s | 1.93 br.s | 8.34–7.24 m |
| **XIf** | *Z* | 5.42 t.q *J* 7.9, *J* 1.1) | 3.69 d (*J* 7.9) | 3.46 s | 1.81 d (*J* 1.1) | 7.40–7.12 m |
| | E | 5.47 t (*J* 8.0) | 3.97 d (*J* 8.0) | 3.50 s | 1.76 br.s | 7.40–7.12 m |
| **XIIc** | *E* | 5.89 t (*J* 8.6) | 3.94 s | 3.66 d (*J* 8.6) | 1.65 br.s | 7.40–7.12 m |

of different polarity. Therewith for a *trans*-adducts occurs simultaneous broadening or narrowing of signals from protons linked to the substituents [12]. We recorded the spectra of compounds **IId** and **Vd** in deuterobenzene and deuterochloroform. The simultaneous broadening of proton signals related to the substituents confirmed *trans*-configuration of the substituents in the adducts **II** and **V**. The structure of compounds **VII–XII** was established basing on published data [2, 3, 5] and on $^1$H–$^1$H coupling constants (Tables 10–15). Besides we measured mass spectra of all compounds synthesized. The identification was performed either by the search in the databases or by analysis of mass spectra proceeding from the main laws of organic compounds fragmentation under the electron impact [13]. The main trends in fragmentation of compounds **I–VI** and **VII–XII** are given below.

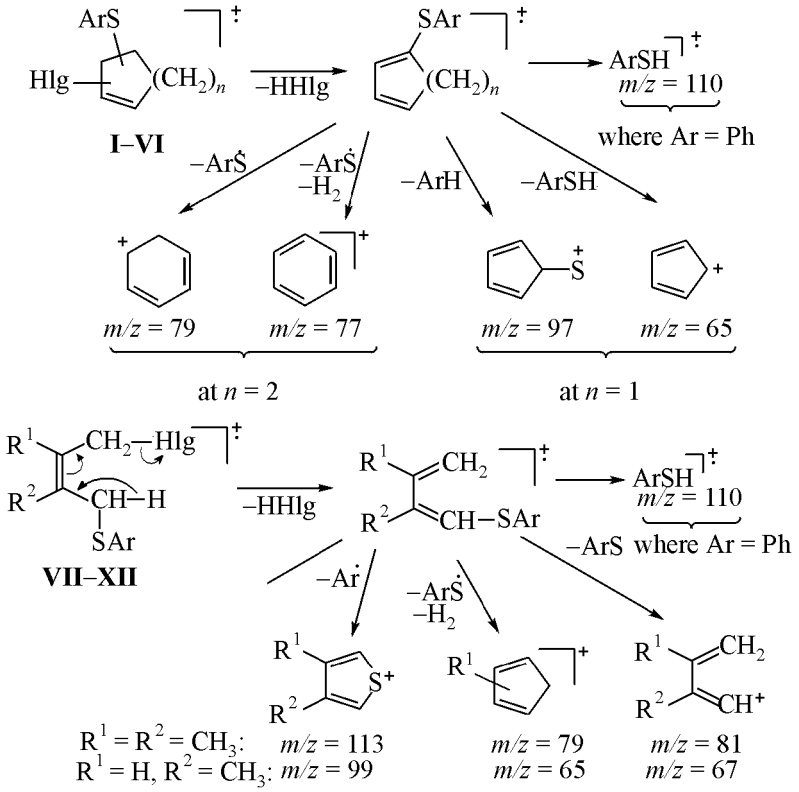


**Table 16.** Parameters of mass spectra of compounds **I**–**XII**

| Compd. no. | Main peaks in mass spectra, *m/z* ($I_{rel}$, %) |
|---|---|
| **I, III, IVa** | 45 (23) $[CHS]^+$, 65 (27) $[C_5H_5]^+$, 97 (38) $[C_5H_5S]^+$, 79 (85) $[C_6H_7]^+$, 171 (18), 219 (100) $[M\text{-}HBr]^+$ |
| **I, III, IVb** | 45 (38) $[CHS]^+$, 53 (43) $[C_4H_6]^+$, 65 (27) $[C_5H_5]^+$, 138 (100) $[C_6H_4NOS]^+$, 154 (65), 174 (44), 185 (35), 219 (77) $[M\text{-}HBr]^+$ |
| **I, III, IVc** | 65 (24) $[C_5H_5]^+$, 67 (100) $[C_5H_7]^+$, 77 (5) $[C_6H_5]^+$, 97 (5) $[C_5H_5S]^+$, 110 (85) $[PhSH]^+$, 174 (8) $[M\text{-}HBr]^+$ |
| **I, III, IVd** | 39 (41) $[C_3H_3]^+$, 45 (47) $[CHS]^+$, 65 (51) $[C_5H_5]^+$, 97 (53) $[C_5H_5S]^+$, 128 (25), 171 (34), 219 (100) $[M\text{-}HCl]^+$ |
| **I, III, IVe** | 56 (94) $[C_4H_8]^+$, 77 (100) $[C_6H_5]^+$, 91 (14), 105 (37), 138 (10) $[C_6H_4NOS]^+$, 175 (23) |
| **I, III, IVf** | 45 (21) $[CHS]^+$, 65 (22) $[C_5H_5]^+$, 77 (8) $[C_6H_5]^+$, 97 (29) $[C_5H_5S]^+$, 109 (85) $[PhS]^+$, 141 (32), 174 (100) $[M\text{-}HCl]^+$ |
| **II, V, VIa** | 44 (18) $[CS]^+$, 51 (14) $[C_4H_3]^+$, 65 (8) $[C_5H_5]^+$, 77 (67) $[C_6H_5]^+$, 79 (85) $[C_6H_7]^+$, 111 (24) $[C_6H_7S]^+$, 155 (8), 171 (5), 184 (16), 233 (100) $[M\text{-}HBr]^+$ |
| **II, V, VIb** | 51 (24) $[C_4H_3]^+$, 77 (34) $[C_6H_5]^+$, 92 (10), 125 (10), 139 (24), 152 (18), 167 (100), 184 (52), 231 (32) $[M\text{-}HBr\_H_2]^+$ |
| **II, V, VIc** | 44 (24) $[CS]^+$, 51 (54) $[C_4H_3]^+$, 65 (27) $[C_5H_5]^+$, 77 (99) $[C_6H_5]^+$, 79 (87) $[C_6H_7]^+$, 92 (13), 110 (76) $[PhSH]^+$, 155 (24), 186 (82) $[M\text{-}HBr\text{–}H2]^+$, 188 (100) $[M\text{-}HBr]^{+\cdot}$ |
| **II, V, VId** | 44 (21) $[CS]^+$, 51 (39) $[C_4H_3]^+$, 65 (22) $[C_5H_5]^+$, 77 (99) $[C_6H_5]^+$, 79 (99) $[C_6H_7]^+$, 111 (63) $[C_6H_7S]^+$, 155 (19), 171 (14), 184 (25), 233 (100) $[M\text{-}HCl]^{+\cdot}$, 234 (42) $[M\text{-}Cl]^+$ |
| **II, V, VIe** | 56 (88) $[C_4H_8]^+$, 77 (100) $[C_6H_5]^+$, 105 (36), 118 (7), 138 (10) $[C_6H_4NOS]^+$, 175 (27) |
| **II, V, VIf** | 44 (28) $[CS]^+$, 51 (34) $[C_4H_3]^+$, 65 (19) $[C_5H_5]^+$, 77 (69) $[C_6H_5]^+$, 79 (56) $[C_6H_7]^+$, 110 (54) $[PhSH]^+$, 155 (16), 186 (41) $[M\text{-}HCl\text{–}H2]^{+\cdot}$, 188 (100) $[M\text{-}HCl]^+$ |
| **VII, VIIIa** | 41 (56) $[C_3H_5]^+$, 53 (80) $[C_4H_5]^+$, 65 (21) $[C_5H_5]^+$, 79 (90) $[C_6H_7]^+$, 81 (95) $[C_6H_9]^+$, 99 (47), 113 (22) $[C_6H_9S]^+$, 121 (12), 235 (100) $[M\text{-}HBr]^{+\cdot}$, 236 (29) $[M\text{-}Br]^+$ |
| **VII, VIIIb** | 41 (54) $[C_3H_5]^+$, 53 (70) $[C_4H_5]^+$, 79 (66) $[C_6H_7]^+$, 81 (39) $[C_6H_9]^+$, 138 (100) $[C_6H_4NOS]^+$, 152 (29), 235 (38) $[M\text{-}HBr]^+$ |
| **VIII, VIIIc** | 41 (26) $[C_3H_5]^+$, 53 (26) $[C_4H_5]^+$, 55 (31) $[C_4H_7]^+$, 65 (19) $[C_5H_5]^+$, 79 (30) $[C_6H_7]^+$, 81 (23) $[C_6H_9]^+$, 83 (51), 99 (34), 110 (46) $[PhSH]^+$, 190 (100) $[M\text{-}HBr]^{+\cdot}$, 191 (16) $[M\text{-}Br]^+$ |
| **VII, VIIId** | 41 (45) $[C_3H_5]^+$, 53 (62) $[C_4H_5]^+$, 65 (16) $[C_5H_5]^+$, 79 (77) $[C_6H_7]^+$, 81 (81) $[C_6H_9]^+$, 99 (32), 113 (15) $[C_6H_9S]^+$, 235 (100) $[M\text{-}HCl]^{+\cdot}$, 236 (20) $[M\text{-}Cl]^+$ |
| **VII, VIIIe** | 41 (50) $[C_3H_5]^+$, 53 (68) $[C_4H_5]^+$, 79 (66) $[C_6H_7]^+$, 81 (39) $[C_6H_9]^+$, 106 (22), 138 (100) $[C_6H_4NOS]^+$, 152 (29), 235 (33) $[M\text{-}HCl]^{+\cdot}$, 236 (4) $[M\text{-}Cl]^+$ |
| **VII, VIIIf** | 41 (27) $[C_3H_5]^+$, 53 (33) $[C_4H_5]^+$, 65 (22) $[C_5H_5]^+$, 79 (37) $[C_6H_7]^+$, 81 (23) $[C_6H_9]^+$, 99 (38), 109 (18), 110 (17) $[PhSH]^+$, 190 (100) $[M\text{-}HCl]^{+\cdot}$, 191 (15) $[M\text{-}Cl]^+$ |
| **IX, X, XIa** | 41 (58) $[C_3H_5]^+$, 65 (21) $[C_5H_5]^+$, 67 (94) $[C_5H_7]^+$, 85 (41), 221 (100) $[M\text{-}HBr]^+$, 222 (17) $[M\text{-}Br]^+$ |
| **IX, X, Xb** | 41 (100) $[C_3H_5]^+$, 65 (39) $[C_5H_5]^+$, 67 (71) $[C_5H_7]^+$, 78 (22) $[C_6H_6]^+$, 106 (29), 138 (77) $[C_6H_4NOS]^+$, 156 (49), 221 (43) $[M\text{-}HBr]^{+\cdot}$, 222 (5) $[M\text{-}Br]^+$ |
| **IX, X, XI, XIIc** | 41 (20) $[C_3H_5]^+$, 51 (19) $[C_4H_3]^+$, 65 (38) $[C_5H_5]^+$, 77 (11) $[C_6H_5]^+$, 99 (82) $[C_5H_7S]^+$, 176 (100) $[M\text{-}HBr]^{+\cdot}$, 177 (11) $[M\text{-}Br]^+$ |
| **IX, X, XId** | 41 (58) $[C_3H_5]^+$, 65 (38) $[C_5H_5]^+$, 67 (70) $[C_5H_7]^+$, 85 (42), 221 (100) $[M\text{-}HCl]^+$, 222 (17) $[M\text{-}Cl]^+$ |
| **IX, X, XIe** | 41 (91) $[C_3H_5]^+$, 65 (42) $[C_5H_5]^+$, 67 (82) $[C_5H_7]^+$, 78 (20) $[C_6H_6]^+$, 106 (32), 138 (100) $[C_6H_4NOS]^+$, 156 (52), 221 (58) $[M\text{-}HCl]^{+\cdot}$, 222 (6) $[M\text{-}Cl]^+$ |
| **IX, X, XIf** | 41 (18) $[C_3H_5]^+$, 51 (19) $[C_4H_3]^+$, 65 (35) $[C_5H_5]^+$, 77 (13) $[C_6H_5]^+$, 99 (98) $[C_5H_7S]^+$, 176 (100) $[M\text{-}HCl]^{+\cdot}$, 177 (17) $[M\text{-}Cl]^+$ |

It should be noted that in the mass spectra of all compounds **I**–**XII** the molecular ion peak is lacking. The main primary decomposition direction of compounds **I**–**XII** is elimination of HHlg molecule resulting in appearance of peaks with *m/z* 219 (**I, III, IVa, b, d, e**), 174 (**I, III, IVc, f**), 233 (**II, V, VIa, b, d, e**), 188 (**II, V, VIc, f**), 235 (**VII, VIIIa, b, d, e**), 190 (**VII, VIIIc, f**), 221 (**IX, X, XIa, b, d, e**), 176 (**IX, X, XIc, f, XIIc**). In the spectra of the majority of compounds the most abundant peak is $[M\text{-}HHlg]^{+\cdot}$ (Table 16). Further character of $[M\text{-}HHlg]^{+\cdot}$ fragmentation is dissimilar and depends on the compound structure.

The fragmentation of $[M\text{-}HHlg]^{+\cdot}$ ions arising from the sulfenylation products of 1,3-cyclohexadiene (**II, V, VI**) consists in elimination of $ArS^{\cdot}$ and $H_2$. resulting in appearance of strong peaks with *m/z* 77 $[C_6H_5^+]$ and 79 $[C_6H_7^+]$, whereas the fragmentation of ions $[M\text{-}HHlg]^{+\cdot}$ from compounds **I, III, IV** occurs with elimination of ArH and ArSH to give ions $[C_5H_5S^+]$, *m/z* 97, and $[C_5H_5^+]$, *m/z* 65.

The fragmentation of ions $[M\text{-}HHlg]^{+\cdot}$ belonging to the sulfenylation products of the open-chain conjugated dienes (2,3-dimethyl-1,3-butadiene and isoprene) occurs by successive ejection of $ArS^{\cdot}$ and $H_2$.

As a result form ions $[C_6H_9^+]$, *m/z* 81, and $[C_6H_7^+]$, *m/z* 79, from compounds **VII, VIIIa–f**, and also $[C_5H_7^+]$, *m/z* 67, and $[C_5H_5^+]$, *m/z* 65, from compounds **IX, X, XIa–f, XIIc**. Besides in the mass spectra of compounds **VII, VIIIa, d** is observed a peak $[C_6H_9S^+]$, *m/z* 113, and for compounds **IX, X, XI, XIIc, IX, X, XIf** appears a peak $[C_5H_7S^+]$, *m/z* 99 originating apparently from the rupture of C–S bond in $[M\text{-}HHlg]^+$ followed by ejection of $Ar^{\cdot}$.

The presence of substituents in the benzene ring linked to the sulfur atom and their position also affects further fragmentation of ions $[M\text{-}HHlg]^{+\cdot}$. A characteristic peak in the mass spectra of all products obtained by dienes sulfenylation with *N*-phenylsulfanylmorpholine **I–VIIIc, f** is that with *m/z* 110 $[C_6H_5SH^+]$, whereas in compounds **I–XIb, e** the nitro group in the *ortho*-position of the benzene ring is responsible for the specificity of their fragmentation ("*ortho*-effect" [13]) and for appearance in the spectra of these compounds of a peak with *m/z* 138 $[C_6H_4NOS^+]$.

## EXPERIMENTAL

Commercial 2,3-dimethyl-1,3-butadiene, isoprene, and 1,3-cyclohexadiene (Lancaster) were used without additional purification. 1,3-Cyclopentadiene was prepared just before use from its dimer (Lancaster) by thermal decomposition along procedure [14]. Arylsulfenamides were prepared by procedure [15] from the corresponding arylsulfenyl chlorides and morpholine. Arylsulfenylchlorides were obtained from the corresponding diaryl sulfides and sulfuryl chloride [16].

$^1H$ NMR spectra were registered on Varian VXR-400 spectrometer at operating frequency 400 MHz. GC-MS spectra were measured on JMS-D300 instrument connected to a JMA-2000 computer and HP-5890 chromatograph. The velocity of spectra registering in the range from 10 to 300 *m/z* or from 40 to 450 *m/z* varied from 1 to 2 seconds. The chromatograms were recorded according to the total ion current. The standard conditions for measuring mass spectra are as follows: ion source temperature 150°C, ionizing electrons energy 70 eV, accelerating voltage 3 kV, mass numbers range 40–400 amu.

Chromatographic analyses were performed on micropacked columns of $50 \times 0.1$, $70 \times 0.1$, $70 \times 0.08$, $120 \times 0.1$ cm and on capillary column of 30 m × 0.53 mm with a low polar phase DB-5 (5% of phenylmethylsilicone), film thickness 1.5 μm. The packing used was Sterling MT of specific surface 7.6 $m^2 g^{-1}$ and grain diameter 0.14–0.16, 0.16–0.18, 0.20–0.22 mm. Helium was applied as carrier gas, flow rate 5 20 $ml\,min^{-1}$ for micropacked columns and 2 $ml\,min^{-1}$ for capillary column The chromatographic separation was carried out on the chromatograph HP-5890 connected to mass spectrometer, at the use of the capillary column division was 1 : 10. The chromatographic separation was optimized by variation of oven temperature programming: from 1 to 25 deg $min^{-1}$ with the micropacked columns to 0.5 to 15 deg $min^{-1}$ for the capillary column.

**Reactions of sulfenamides with dienes in the presence of phosphorus oxyhalides.** To a solution of sulfenamide (2 mmol) in anhydrous $CH_2Cl_2$ (15 ml) while vigorous stirring at –40°C was slowly added a solution of 2 mmol of phosphorus oxyhalide in the same solvent (15 ml), and the mixture was stirred for 10 min. Then a solution of diene (3 mmol) in anhudrous $CH_2Cl_2$ (20 ml) was slowly added, the mixture was stirred till the completion of the reaction [TLC monitoring on fixed silica gel layer (Silufol)]. The reaction mixture was filtered through a 7 cm bed of silica gel, and the solvent was evaporated.

Data on yields and composition of the reaction products are compiled in Tables 1–4. Chemical shifts of $^1H$ nuclei (ppm) and coupling constants $^1H$–$^1H$ (Hz) of the compounds are listed in Tables 5–15. Parameters of mass spectra are presented in Table 16.

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