Reaction of bicyclo[2.2.1]hepta-2,5-diene with the arenesulfenamide—phosphorus(v) oxohalide system: chemo-, regio-, and steroselectivity

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The chemo-, regio- and stereoselectivities of electrophilic sulfenylation of bicyclo[2.2.1]hepta-2,5-diene with arenesulfenamides activated by phosphorus(v) oxohalides were studied. The ratio of the products of *endo*- to *exo*-attack of the diene by the electrophilic species depends on the solvent nature. The proportions of the products formed upon addition to one double bond and upon homoallylic participation of the second double bond depend on solvent polarity, the nature of the halogen, the substituents in the sulfenamide benzene ring, and on the reaction time. In addition, the formation of mixed adducts was proven for the reaction carried out in acetonitrile and the formation of disulfenylation products was found in the reaction with excess sulfenylating reagent. Isomerization of *exo*-3-arylthio-*endo*-2-halobicyclo[2.2.1]hept-5-enes to the products formed with homoallylic participation of the second double bond, *exo*-5-arylthio-*endo*-3-halotricyclo[2.2.1.$0^{2,6}$]heptanes, was shown to be possible.

Key words: arenesulfenamides, phosphorus(v) oxohalides, bicyclo[2.2.1]hepta-2,5-diene, sulfenylation, isomerization.

The new method of halosulfenylation of unsaturated compounds with the arenesulfenamide—phosphorus oxohalide system proposed in our previous study[1] gave good results for alkenes[1] and alkynes.[2] Owing to high yields and ready availability and stability of the initial reactants, this method may be regarded as an alternative to the existing methods of chloro- and bromosulfenylation of unsaturated compounds (see, for example, Refs. 3—12). To continue our research, we studied the reaction of arenesulfenamides activated by phosphorus(v) oxohalides with bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), which is a convenient substrate for elucidation of the reaction mechanisms.

Results and Discussion

We studied reactions of norbornadiene (**1**) with *N*-(*p*-nitrophenylthio)morpholine (**2a**), *N*-(*o*-nitrophenylthio)morpholine (**2b**), and *N*-phenylthiomorpholine (**2c**) in the presence of phosphorus oxochloride (**3a**) and oxobromide (**3b**) in various solvents (Scheme 1). These reactions in CH_2Cl_2 and AcOEt give isomeric β- (**4**, **5**) and γ-halosulfides (**6**, **7**). In MeCN, γ-*N*-acetamidosulfides **8** and **9** are formed apart from halosulfides.

Data on the product yields and ratios are listed in Table 1.

Arenesulfenamides as such are weak electrophiles unable to add to multiple bonds; however, on treatment with $POCl_3$ or $POBr_3$, they form active complexes, which we identify conventionally as having structure **10** where the positive charge on sulfur is higher than in the initial sulfenamide[1] (Scheme 2).

The ^1H and ^{13}C NMR spectra recorded for a mixture of *N*-(*p*-nitrophenylthio)morpholine (**2a**)—phosphorus oxochloride (**3a**) (1 : 1) in $CDCl_3$ contain signals of the initial sulfenamide **2a** and an additional set of signals for the aromatic system and the morpholine ring, which we attribute to the formation of complex **10** (Table 2). After addition of the olefin, the signals assigned to complex **10** disappear over a period of several minutes being replaced by sets of signals due to the product of addition at the C=C bond and phosphorous acid monoamide dichloride **11** (see Table 2 and Experimental).

Previously,[15] it was shown that in the case of thiobismorpholine, phosphorus oxohalide is coordinated to one N atom; the ^1H and ^{13}C NMR spectra exhibit signals for two nonequivalent morpholine rings, one exhibiting spin-spin coupling constants with the phosphorus nucleus. The absence of spin-spin coupling constants for the ^1H or ^{13}C nuclei of the morpholine ring with the ^{31}P nuclei in this particular case of sulfenamide activation is an argument for the assumption that in complex **10**, phos-

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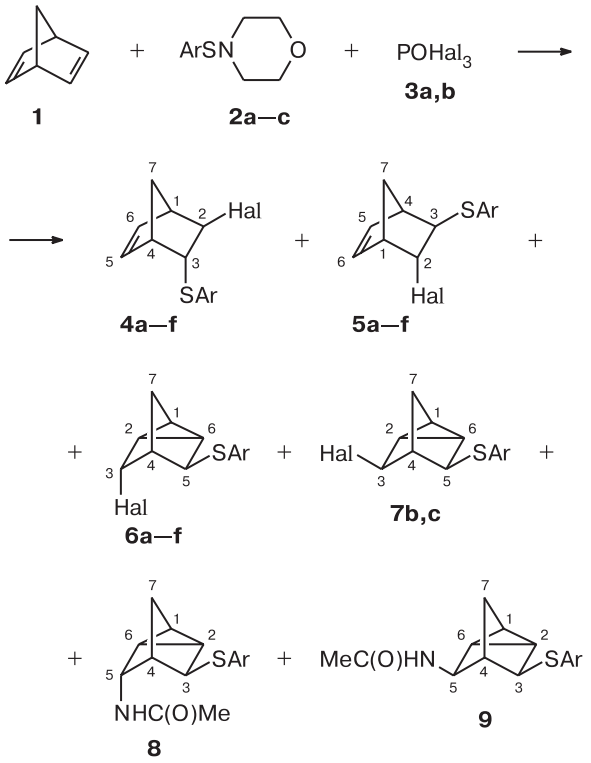
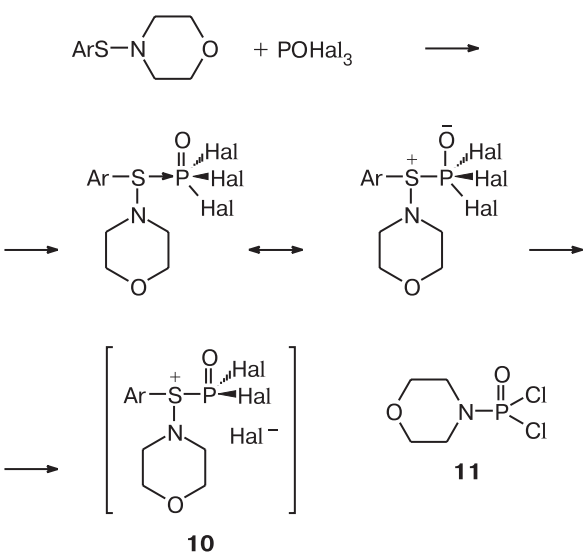
Scheme 1



2: Ar = 4-$NO_2C_6H_4$ (**a**), 2-$NO_2C_6H_4$ (**b**), Ph (**c**)
3: Hal = Cl (**a**), Br (**b**)
4—7: Hal = Cl (**a—c**), Br (**d—f**);
Ar = 4-$NO_2C_6H_4$ (**a, d**), 2-$NO_2C_6H_4$ (**b, e**), Ph (**c, f**)
8, 9: Ar = 2-$NO_2C_6H_4$

Scheme 2



phorus oxohalide is coordinated to the sulfenamide S atom (Fig. 1) rather than to the N atom. Data of PM3 semiempirical quantum-mechanical calculations are consistent with the assumption that phosphorus oxohalide is coordinated to the S atom of sulfenamide. The optimized geometry of complex **10** is shown in Fig. 1.

The addition of complex **10** to norbornadiene (**1**) yields an intermediate that can be successfully described in terms of the ion-pair mechanism concept, which has been widely discussed previously.[16,17]

Table 1. Product yields in the reactions of arenesulfenamides **2a—c** activated by phosphorus(v) oxohalides with bicyclo[2.2.1]hepta-2,5-diene (**1**) (the yields of similar products obtained in the sulfenylation of the same olefin with arylsulfenyl chloride are given for comparison[13])

Sulfenamide	$POHal_3$	Solvent	t [a]/h	Products[b] (%)							Overall yield (%)
				of the *endo*-attack	of the *exo*-attack					Ar_2S	
				4	**5**	**6**	**7**	**8**	**9**		
2a	**3a**	CH_2Cl_2	2	30	11	59	—	—	—	—	78
2b	**3a**	CH_2Cl_2	2	20	24	56	—	—	—	—	78
2c	**3a**	CH_2Cl_2	3	23	47	30	—	—	—	—	34
2a	**3b**	CH_2Cl_2	1.5	20	40	40	—	—	—	—	100
2b	**3b**	CH_2Cl_2	1.5	22	43	35	—	—	—	—	76
2c	**3b**	CH_2Cl_2	4	23	57	19	—	—	—	—	43
2b	**3a**	CH_2Cl_2	48	18	14	47	19	—	—	—	78
2c	**3a**	CH_2Cl_2	120	23	—	57	20	—	—	—	34
2b	**3a**	AcOEt	2	31	44	25	—	—	—	—	57
2b	**3a**	MeCN	2	17	—	2	—	21	49	11 [c]	47
2b	**3a**	MeCN [d]	2	39	—	4	—	13	30	14 [c]	50
2-NO_2-C_6H_4SCl		CCl_4		20	70	10	—	—	—	—	81

[a] Reaction time.
[b] Approximate contents of products in the reaction mixture determined from ^1H NMR spectroscopy data are given.
[c] R_f 0.33 (AcOEt—petroleum ether, 1 : 3), m.p. 119—121 °C (*cf.* Ref. 14: m.p. 122—123 °C).
[d] The reaction was carried out in the presence of $LiClO_4$ (doping conditions).

Table 2. ^{1}H and ^{13}C NMR spectra of compounds **2a**, **11** and sulfenylating reagents **10**, **14** in $CDCl_3$ (for compounds **2a**, **10**, **11**) or CD_3CN (for compound **14**)

Compound	δ_H ($J_{H,H}$/Hz)		δ_C	
	O_2N–C$_6$H$_4$–S–	–N(CH$_2$)$_2$O(CH$_2$)$_2$	O_2N–C$_6$H$_4$–S–	–N(CH$_2$)$_2$O(CH$_2$)$_2$
2a	8.15, 7.42 (J = 9.0)	3.79, 3.10 (J = 4.7)	149.9, 145.0, 123.7, 122.4	67.5, 56.0
10	8.22, 7.58 (J = 9.1)	3.96, 3.21 (J = 4.3)	146.6, 144.4, 125.6, 123.9	63.5, 43.3
11	—	3.68 (dt, 4 H, J = 4.9, $J_{H,P}$ = 2.1); 3.28 (dt, 4 H, J = 4.9, $J_{H,P}$ = 4.9)	—	65.1 (d, $J_{C,P}$ = 7.4); 44.2 (d, $J_{C,P}$ = 1.4)
14	8.12, 7.74 (J = 9.1)	—	—	—

Note. The ^{1}H NMR spectra of the 4-$NO_2C_6H_4S$ fragment exhibit an AA´BB´ system; the $J_{A,B}$ constant is given. The ^{1}H NMR spectra of the morpholine fragment represent an A_2B_2 system; the $J_{A,B}$ constant is given.

The reactions carried out in solvents with different polarities result in different ratios of the products resulting from *exo*- and *endo*-attacks of the diene system (see Table 1). This can be explained as follows: the *endo*-attack is preferred from the standpoint of electronic factors because in this case, the electrophile can be coordinated simultaneously to two double bonds, while the *exo*-attack is better for steric reasons. Thus, in less polar solvents in which the electrophilic species is less solvated and, hence, less bulky, the reaction should yield a greater amount of the *endo*-attack product than in more polar solvents. Indeed, in AcOEt (ε = 6.02),[18] the *endo*- to *exo*-attack product ratio is 31 : 69, that in CH_2Cl_2 (ε = 8.9)[18] is 20 : 80, while in MeCN (ε = 36.2),[18] this ratio is 17 : 83.

The amount of nortricyclane products formed in the reaction depends also on the nature of the halogen in $POHal_3$. Indeed, when $POCl_3$ is used for activation, the proportion of products **6** is substantially higher than that obtained in the presence of $POBr_3$ (*cf.* rows 1 and 4, 2 and 5, 3 and 6 in Table 1). Apparently, the less bulky and more electronegative chlorine is better solvated by solvent molecules, which shifts equilibrium toward the solvent-separated ion pair and increases the yield of nortricyclane products.

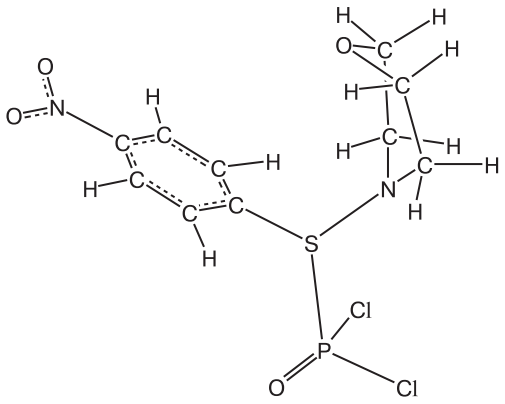


Fig. 1. Structure of the *N*-(*p*-nitrophenylthio)morpholine—phosphorus(v) oxochloride complex from the data of PM3 semiempirical quantum-mechanical calculations.

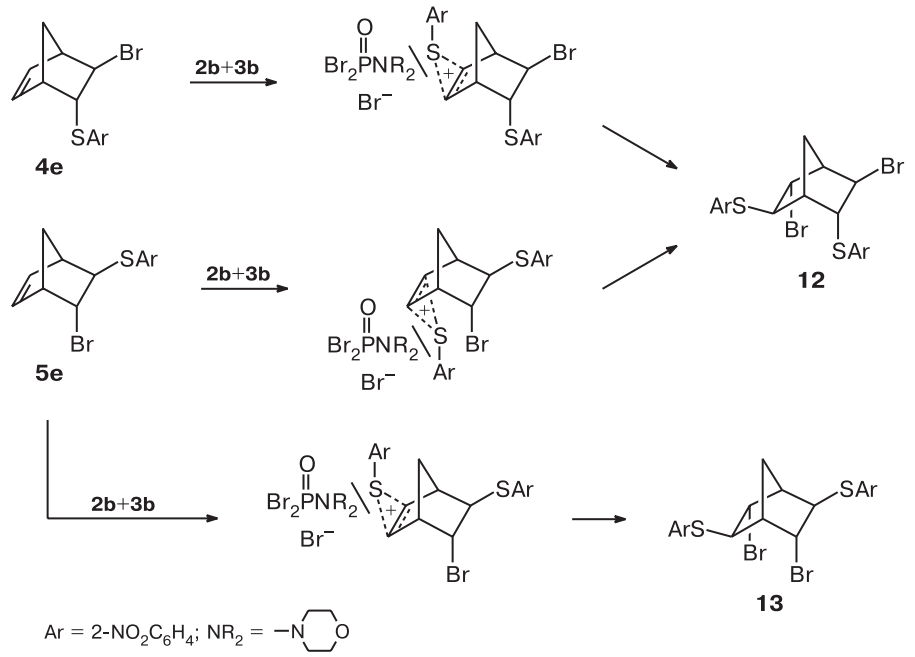
It was found that the proportion of 1,2-adduct **5** in the reaction mixture decreases with time, while the proportion of compound **6** increases, and in some cases, initially missing 3,5-di-*exo*-substituted nortricyclane **7** is also formed. Probably, the formation of product **5** (1,2-*exo*-addition) is reversible, and over a period of two days, thermodynamic equilibrium is established in the reaction mixture, resulting in the set of products we observe.

The possibility of **5** → **6** isomerisation is also confirmed by experiment: on stirring of a 22 : 43 : 35 mixture of **4e**, **5e**, and **6e** with a solution of *N*-(*o*-nitrophenylthio)morpholine (**2b**) activated by $POBr_3$ (**3b**), di(arylthio)dihalonorbornanes **12** and **13**, resulting from addition of the second equivalent of the reagent to the second double bond, were isolated together with compound **6e** (the **6e** : **12** : **13** ratio was 55 : 37 : 8). It is evident that the increase in the content of product **6e** in the mixture is due to transformation of some of alkene **5e** into nortricyclane **6e**.

It should be noted that product **13** could have formed from compound **5e** only in the case of *exo*-attack by the electrophilic species at the second double bond. If **5e** → **4e** isomerization is considered impossible, compound **12** can be formed both from **5e** due to *endo*-attack of the sulfenylating reagent and from **4e** due to *exo*-addition of ArS^+ (Scheme 3).

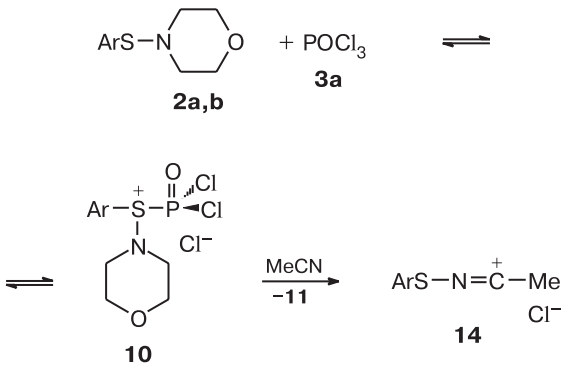
The use of strong electrolytes (for example, $LiClO_4$) as polar additives in olefin sulfenylation increases the medium polarity and, as a consequence, increases the proportion of rearranged products (doping effect).[17] Indeed, when MeCN is used as the solvent in $POHal_3$-activated sulfenylation of norbornadiene, 3-arylthio-5-*N*-acetamidotricyclo[2.2.1.0^{2,6}]heptanes **8** and **9** are formed

Scheme 3



as the major products. However, the formation of substantial amounts (11—14%) of diaryl sulfide (which is not observed when the reaction is carried out in other solvents) and the unexpected ratio of products obtained in the presence of $LiClO_4$ (see Table 1) suggest that in MeCN, the reaction of the arenesulfenamide—phosphorus oxohalide system with norbornadiene (**1**) proceeds *via* the formation of sulfenylating reagent of a different structure. Probably, new sulfenylating complex **14** is formed when complex **10** reacts with MeCN molecule (Scheme 4).

Scheme 4



Thus the ^1H and ^{13}C NMR spectra of a *N*-(*p*-nitrophenylthio)morpholine (**2a**)—phosphorus oxochloride (**3a**) mixture in $CDCl_3$ exhibit signals for the initial sulfenamide and complex **10**, whereas in CD_3CN, apart from these signals, the spectrum contains signals for compound **11** and an additional set of signals, which may be attributed to a new electrophilic complex **14**.

The structures of the reaction products were established by ^1H and ^{13}C NMR spectroscopy (Tables 3—5). Analysis of the spectra and the subsequent structural assignments were based on published data on the influence of substituents on the chemical shifts, on the $^1H—^1H$ spin-spin coupling constants, and on the nuclear Overhauser effect (NOE) data.

The ^1H NMR spectra of products **4** and **5** (see Table 3) contain signals of olefinic protons, and the magnitude of the spin-spin coupling constant for the protons at substituents ($J_{2,3}$ = 2.6—3.4 Hz) indicates that these compounds result from 1,2-addition to one double bond and attests to *trans*-positions of the arylthio group and the halogen atom, because *trans*-vicinal derivatives of norbornane are normally characterized by $J_{2,3}$ = 2.5—5.0 Hz, while for *cis*-derivatives, $J_{2,3}$ = 6—10 Hz.[18] The spectroscopic characteristics of compounds **4** and **5** correspond to those reported previously.[16]

Products **6b** and **7b** were isolated as a mixture. The signals for the H(3) and H(5) protons in the major isomer **6b** occur at δ 4.12 and 4.08, respectively. In the case of isomer **7b**, these signals are at about δ 4.04 and 3.36. As shown previously,[19] a substantial upfield shift of the H(5) signal is due to a change in the orientation (*endo*→*exo*) of the substituent at C(3). This suggests that compound **6b** is *exo*-5-(*o*-nitrophenylthio)-*endo*-3-chlorotricyclo[2.2.1.$0^{2,6}$]heptane, and **7b** is *exo*-5-(*o*-nitrophenylthio)-*exo*-3-chlorotricyclo[2.2.1.$0^{2,6}$]heptane.

Table 3. ^{1}H NMR spectra of compounds **4—13** in $CDCl_3$

Compound	δ ($J_{H,H}$/Hz)							
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7), H(7′)	Other signals
4a	3.17 (br.s)	3.81 (t, $J_{2,3} \approx J_{2,7'} = 2.8$)	3.71 (t, $J_{3,2} \approx J_{3,4} = 2.3$)	3.13 (br.s)	6.23 (dd, $J_{5,6} = 5.7$, $J_{5,4} = 3.3$)	6.31 (dd, $J_{6,5} = 5.7$, $J_{6,1} = 2.9$)	2.10 (dt, $J_{7,7'} = 9.4$, $J_{7,1} = J_{7,4} = 1.3$); 1.85 (dq, $J_{7,7'} = 9.4$, $J_{7',1} = J_{7',4} = J_{7',2} = 1.9$)	8.12, 7.48 [a]
4b	3.19 (br.s)	3.79 (t, $J_{2,3} \approx J_{2,7'} = 2.9$)	3.75 (t, $J_{3,2} \approx J_{3,4} = 2.1$)	3.14 (br.s)	6.22 (dd, $J_{5,6} = 5.6$, $J_{5,4} = 3.2$)	6.37 (dd, $J_{6,5} = 5.6$, $J_{6,1} = 2.7$)	2.11 (d, $J_{7,7'} = 9.3$); 1.85 (dq, $J_{7,7'} = 9.3$, $J_{7',1} = J_{7',4} = J_{7',2} = 1.8$)	8.14, 7.82, 7.59, 7.25 [b]
4c	3.05 (br.s)	3.66 (t, $J_{2,3} \approx J_{2,7'} = 2.1$)	3.64 (t, $J_{3,2} \approx J_{3,4} = 2.9$)	3.02 (br.s)	6.16 (dd, $J_{5,6} = 5.3$, $J_{5,4} = 3.0$)	6.29 (dd, $J_{6,5} = 5.3$, $J_{6,1} = 3.0$)	1.97 (d, $J_{7,7'} = 9.3$); 1.75 (dq, $J_{7,7'} = 9.2$, $J_{7',1} = J_{7',4} = J_{7',2} = 1.8$)	7.44—7.25 (m)[c]
4d	3.20 (br.s)	3.97 (t, $J_{2,3} \approx J_{2,7'} = 3.0$)	3.66 (t, $J_{3,2} \approx J_{3,4} = 2.4$)	3.16 (br.s)	6.22 (dd, $J_{5,6} = 5.6$, $J_{5,4} = 3.3$)	6.28 (dd, $J_{6,5} = 5.6$, $J_{6,1} = 2.7$)	2.14 (d, $J_{7,7'} = 9.5$); 1.87 (dq, $J_{7,7'} = 9.5$, $J_{7',1} = J_{7',4} = J_{7',2} = 1.9$)	8.12, 7.48 [a]
4e	3.24 (br.s)	3.95 (t, $J_{2,3} \approx J_{2,7'} = 2.9$)	3.72 (t, $J_{3,2} \approx J_{3,4} = 2.4$)	3.19 (br.s)	6.22 (dd, $J_{5,6} = 5.4$, $J_{5,4} = 3.0$)	6.36 (dd, $J_{6,5} = 5.4$, $J_{6,1} = 2.8$)	2.17 (d, $J_{7,7'} = 9.4$); 1.88 (d, $J_{7,7'} = 9.4$)	8.13, 7.84 7.57, 7.26 [b]
4f	3.14 (br.s)	3.82 (t, $J_{2,3} \approx J_{2,7'} = 3.2$)	3.64 (t, $J_{3,2} \approx J_{3,4} = 2.7$)	3.05 (br.s)	5.95 (dd, $J_{5,6} = 5.6$, $J_{5,4} = 3.1$)	6.18 (dd, $J_{6,5} = 5.6$, $J_{6,1} = 3.4$)	2.05 (d, $J_{7,7'} = 9.2$); 1.80 (dq, $J_{7,7'} = 9.2$, $J_{7',1} = J_{7',4} = J_{7',2} = 2.0$)	7.50—7.15 (m)[c]
5a	3.22 (br.s)	4.20 (t, $J_{2,3} \approx J_{2,1} = 3.4$)	3.19 (t, $J_{3,2} \approx J_{3,7'} = 3.0$)	2.94 (br.s)	6.28 (dd, $J_{5,6} = 5.6$, $J_{5,4} = 2.9$)	6.41 (dd, $J_{6,5} = 5.6$, $J_{6,1} = 3.1$)	1.83 (d, $J_{7,7'} = 9.6$); 1.76 (dq, $J_{7,7'} = 9.6$, $J_{7',1} = J_{7',4} = J_{7',3} = 1.9$)	8.12, 7.43 [a]
5b	3.22 (br.s)	4.24 (t, $J_{2,3} \approx J_{2,1} = 3.2$)	3.16 (t, $J_{3,2} \approx J_{3,7'} = 3.0$)	2.97 (br.s)	6.29 (dd, $J_{5,6} = 5.7$, $J_{5,4} = 2.7$)	6.44 (dd, $J_{6,5} = 5.7$, $J_{6,1} = 3.2$)	1.88 (d, $J_{7,7'} = 10.2$); 1.74 (dq, $J_{7,7'} = 10.2$, $J_{7',1} = J_{7',4} = J_{7',3} = 1.9$)	8.18, 7.62, 7.56, 7.28 [b]
5c	3.11 (br.s)	4.16 (t, $J_{2,3} \approx J_{2,1} = 3.2$)	3.05 (t, $J_{3,2} \approx J_{3,7'} = 3.1$)	2.83 (br.s)	6.17 (dd, $J_{5,6} = 5.7$, $J_{5,4} = 2.8$)	6.29 (dd, $J_{6,5} = 5.7$, $J_{6,1} = 3.0$)	1.84 (d, $J_{7,7'} = 9.3$); 1.66 (dq, $J_{7,7'} = 9.3$, $J_{7',1} = J_{7',4} = J_{7',3} = 2.6$)	7.44—7.25 (m)[c]

(*to be continued*)

Table 3 (*continued*)

Compound	δ ($J_{H,H}$/Hz)							
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7), H(7′)	Other signals
5d	3.24 (br.s)	4.13 (t, $J_{2,3} \approx J_{2,1} = 3.2$)	3.28 (t, $J_{3,2} \approx J_{3,7'} = 2.8$)	2.92 (br.s)	6.23 (dd, $J_{5,6} = 5.6$, $J_{5,4} = 2.9$)	6.39 (dd, $J_{6,5} = 5.6$, $J_{6,1} = 3.2$)	1.82 (d, $J_{7,7'} = 9.5$); 1.73 (m)	8.12, 7.42 [a]
5e	3.26 (br.s)	4.19 (t, $J_{2,3} \approx J_{2,1} = 3.3$)	3.26 (t, $J_{3,2} \approx J_{3,7'} = 2.8$)	2.96 (br.s)	6.27 (dd, $J_{5,6} = 5.7$, $J_{5,4} = 2.9$)	6.43 (dd, $J_{6,5} = 5.7$, $J_{6,1} = 3.2$)	1.88 (d, $J_{7,7'} = 9.4$); 1.74 (dq, $J_{7,7'} = 9.4$, $J_{7',1} = J_{7',4} = J_{7',3} = 2.3$)	8.18, 7.63, 7.57, 7.27 [b]
5f	3.18 (br.s)	4.12 (t, $J_{2,3} \approx J_{2,1} = 3.4$)	3.16 (t, $J_{3,2} \approx J_{3,7'} = 3.0$)	2.84 (br.s)	6.16 (dd, $J_{5,6} = 5.7$, $J_{5,4} = 2.7$)	6.31 (dd, $J_{6,5} = 5.7$, $J_{6,1} = 3.2$)	1.85 (d, $J_{7,7'} = 9.5$); 1.66 (dq, $J_{7,7'} = 9.5$, $J_{7',1} = J_{7',4} = J_{7',3} = 2.2$)	7.50—7.15 (m)[c]
6a	1.53 (tq, $J_{1,2} = J_{1,6} = 5.2$, $J_{1,7} = J_{1,7'} = J_{1,4} = 1.0$)	1.66 (tt, $J_{2,1} = J_{2,6} = 5.2$, $J_{2,3} = J_{2,4} = 1.1$)	4.15 (br.s)	2.26 (br.s)	4.10 (t, $J_{5,4} = J_{5,6} = 1.6$)	1.62 (tt, $J_{6,1} = J_{6,2} = 5.2$, $J_{6,5} = J_{6,4} = 1.1$)	1.96 (dt, $J_{7,7'} = 11.5$, $J_{7,1} = J_{7,4} = 1.5$); 1.52 (dt, $J_{7,7'} = 11.5$, $J_{7',1} = J_{7',4} = 1.2$)	8.12, 7.38 [a]
6b	1.54 (tq, $J_{1,2} = J_{1,6} = 5.0$, $J_{1,7} = J_{1,7'} = J_{1,4} = 1.9$)	1.62 (m)	4.12 (t, $J_{3,2} = J_{3,4} = 1.6$)	2.30 (br.s)	4.08 (br.s)	1.65 (m)	2.02 (dt, $J_{7,7'} = 11.3$, $J_{7,1} = J_{7,4} = 1.3$); 1.50 (dt, $J_{7,7'} = 11.3$, $J_{7',1} = J_{7',4} = 1.4$)	8.18, 7.57, 7.56, 7.24 [b]
6c	1.47 (m)	1.57 (d, $J_{2,1} = 5.1$)	4.00 (br.s)	2.14 (br.s)	3.96 (br.s)	1.57 (d, $J_{6,1} = 5.1$)	2.03 (dt, $J_{7,7'} = 11.3$, $J_{7,1} = J_{7,4} = 1.5$); 1.44 (d, $J_{7,7'} = 11.3$)	7.44—7.25 (m)[c]
6d	1.46 (t, $J_{1,2} = J_{1,6} = 5.2$)	1.73 (t, $J_{2,1} = J_{2,6} = 5.2$)	4.13 (br.s)	2.29 (br.s)	4.10 (t, $J_{5,4} = J_{5,6} = 1.4$)	1.62 (t, $J_{6,1} = J_{6,2} = 5.2$)	1.91 (dt, $J_{7,7'} = 11.6$, $J_{7,1} = J_{7,4} = 1.4$); 1.51 (d, $J_{7,7'} = 11.6$)	8.12, 7.48 [a]
6e	1.64 (tq, $J_{1,2} = J_{1,6} = 5.4$, $J_{1,7} = J_{1,7'} = J_{1,4} = 1.1$)	1.47 (t, $J_{2,1} = J_{2,6} = 5.4$)	4.11 (br.s)	2.33 (br.s)	4.09 (br.s)	1.72 (t, $J_{6,1} = J_{6,2} = 5.4$)	1.97 (dt, $J_{7,7'} = 11.2$, $J_{7,1} = J_{7,4} = 1.4$); 1.50 (d, $J_{7,7'} = 11.3$)	8.18, 7.60 7.57, 7.25 [b]
6f	1.40 (tq, $J_{1,2} = J_{1,6} = 5.2$, $J_{1,7} = J_{1,7'} = J_{1,4} = 1.1$)	1.57 (tt, $J_{2,1} = J_{2,6} = 5.2$, $J_{2,3} = J_{2,4} = 1.1$)	4.04 (t, $J_{3,2} \approx J_{3,4} = 1.6$)	2.20 (br.s)	4.04 (br.s)	1.64 (m)	2.00 (dt, $J_{7,7'} = 11.1$, $J_{7,1} = J_{7,4} = 1.6$); 1.44 (dt, $J_{7,7'} = 11.3$, $J_{7',1} = J_{7',4} = 1.4$)	7.50—7.15 (m)[c]
7b	1.54 (tq, $J_{1,2} = J_{1,6} = 5.0$, $J_{1,7} = J_{1,7'} = J_{1,4} = 1.9$)	1.59 (d, $J_{2,1} = 5.0$)	4.04 (t, $J_{3,2} = J_{3,4} = 1.7$)	2.40 (br.s)	3.36 (br.s)	1.59 (d, $J_{6,1} = 5.0$)	2.02 (m, 2 H)	8.15, 7.48, 7.55, 7.25 [b]

(*to be continued*)

Table 3 (*continued*)

Compound	δ ($J_{H,H}$/Hz)							
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7), H(7′)	Other signals
7c	1.51 (tt, $J_{1,2} = J_{1,6} =$ 5.0, $J_{1,7} =$ $J_{1,7'} = 1.2$	1.53 (d, $J_{1,2} = 5.1$)	3.89 (t, $J_{3,2} \approx$ $J_{3,4} = 1.6$)	2.14 (br.s)	3.22 (br.s)	1.53 (d, $J_{6,1} = 5.1$)	2.00 (m, 2 H)	7.44—7.25 (m)[c]
8	1.45 (tq, $J_{1,2} =$ $J_{1,6} = 5.0$, $J_{1,7} = J_{1,7'} =$ $J_{1,4} = 1.0$)	1.37 (tt, $J_{2,1} =$ $J_{2,6} = 5.0$, $J_{2,3} =$ $J_{2,4} = 1.2$)	3.63 (s)	2.45 (br.s)	3.99 (d, $J_{5,NH} =$ 6.3)	1.51 (m)[d]	1.98 (m) 1.52 (m)[d]	8.14, 7.54, 7.54, 7.24 [b] 6.44 (d, 1 H, NH, $J_{5,NH} =$ 5.7); 2.05 (s, 3 H, Me)
9	1.45 (tq, $J_{1,2} =$ $J_{1,6} = 5.0$, $J_{1,7} = J_{1,7'} =$ $J_{1,4} = 1.0$)	1.39 (tt, $J_{2,1} =$ $J_{2,6} = 5.0$, $J_{2,3} =$ $J_{2,4} = 1.2$)	3.42 (s)	2.32 (br.s)	4.00 (dt, $J_{5,NH} = 7.4$, $J_{5,4} =$ $J_{5,6} = 1.5$)	1.48 (m)[d]	1.91 (dt, $J_{7,7'} = 11.5$, $J_{7,1} =$ $J_{7,4} = 1.3$); 1.45 (m)[d]	8.14, 7.54, 7.54, 7.24 [b] 5.56 (d, 1 H, NH, $J_{5,NH} = 6.9$); 1.93 (s, 3 H, Me)
12	2.94 (d, $J_{1,6} = 4.8$)	4.58 (dd, $J_{2,3} = 4.3$, $J_{2,7} = 2.1$)	4.11 (m)[e]	2.66 (d, $J_{4,3} =$ 2.9)	4.02 (dd, $J_{5,6} = 4.8$, $J_{5,7'} = 2.6$)	4.15 (t, $J_{6,5} =$ $J_{6,1} = 4.3$)	2.28 (d, $J_{7,7'} = 11.8$); 2.17 (d, $J_{7',7} = 11.8$)	8.03—7.00 (m)[b]
13	2.63 (d, $J_{1,6} = 5.0$)	4.24 (t, $J_{2,3} \approx$ $J_{2,1} = 4.5$)	4.11 (m)[e]	2.63 (d, $J_{4,3} =$ 5.0)	4.24 (t, $J_{5,6} \approx$ $J_{5,4} = 4.5$)	4.11 (m)[e]	1.98 (br.s, 2 H)[d]	8.03—7.00 (m)[b]

[a] Signals of the 4-$NO_2C_6H_4S$ fragment.
[b] Signals of the 2-$NO_2C_6H_4S$ fragment.
[c] Signals of the C_6H_5S fragment.
[d] The signals in the spectrum overlap.
[e] The signals overlap with the signals of compound **6e**.

Nuclear Overhauser effect experiments confirm this assignment. In product **6b**, irradiation of the signal with δ 4.12 does not induce NOE at the aryl-group protons, which permits this signal to be assigned to the H—C—Cl fragment (see below, for **7b** and **9**). The $\eta_{H(5)}(H(3))$ effect is missing either, but the intensity of the signal of the H(7) proton changes ($\eta_{H(7)}(H(3)) = 2.3\%$). This is possible only in the case of *endo*-orientation of the Cl atom.

The assignment of ^{1}H NMR signals of product **7b** was based on the NOE data (see Table 5) and on comparison with published data.[19] The great effect (5%) at the *ortho*-proton of the aryl group induced by irradiation of the proton with δ 3.36 allows this signal to be assigned unambiguously to the H—C—SAr fragment. The lower-field signal (δ 4.04) was assigned to the H—C—Cl fragment. As has been shown previously,[20] the absence of NOE at H(7) and H(7′) on irradiation of H(3) and H(5)

Table 4. ^{13}C NMR spectra of compounds **6b**, **7b**, **8**, and **9** in $CDCl_3$

Compound	δ							
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C arom.
6b	15.0	20.0	64.8	41.5	47.9	15.9	29.4	137.4, 133.5, 127.0, 126.1, 124.5
7b		19.9	62.7	41.8	48.3		27.7	133.3, 127.4, 126.0, 124.9
8*	13.2	15.7	47.6	38.5	56.4	16.5	29.4	146.0, 137.4, 133.3, 127.3, 125.9, 124.5
9**	11.7	16.4	48.6	38.6	54.5	16.7	27.0	146.0, 136.9, 133.4, 127.5, 125.8, 124.6

* 171.0 (CO), 23.2 (Me).
** 170.0 (CO), 23.2 (Me).

Table 5. NOE data (η) for compounds **7b** and **9** (in $CDCl_3$)

Compound	Irradiated protons	Observed protons, η (%)							
		H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	NH	2-$NO_2C_6H_4$
7b	H(3)CCl	2.9	—	2.8	8.1	—	—	—	—
	H(5)CS	—	10.4	1.7	—	3.3	—	—	5.0
9	H(3)CS	5.4	—	2.4	10.3	—	—	—	5.6
	H(5)CN	—	9.3	2.5	—	4.5	—	0.9	—
	NH	—	—	—	1.6	2.3	4.1	—	—

and the high $\eta_{H(3)}(H(5))$ and $\eta_{H(5)}(H(3))$ values (~9%) imply a spatial proximity of these protons and confirm unambiguously the di-*exo*-configuration of compound **7b**.

A similar change in the chemical shifts of H(3) and H(5) observed for the whole series of products **6** and **7** (see Table 3) makes it possible to identify products **6** as *exo*-5-arylthio-*endo*-3-halotricyclo[2.2.1.$0^{2,6}$]heptanes and **7**, as *exo*-5-arylthio-*exo*-3-halotricyclo[2.2.1.$0^{2,6}$]heptanes.

Compounds **8** and **9** were also isolated and characterized as a mixture. The chemical shifts of protons at substituents correspond to correlations reported previously.[19] Structure **9** is additionally confirmed by NOE experiment (see Table 5); these data provided unambiguous assignment of signals in the ^{1}H NMR spectrum and a proof for the di-*exo*-configuration of product **9**.

The structure of compound **12** was established using analysis of the chemical shifts and spin-spin coupling constants in the ^{1}H NMR spectrum. Thus the $J_{2,3}$ = 4.3 Hz and $J_{5,6}$ = 4.8 Hz values correspond to *trans*-positions of the H(2) and H(3), H(5) and H(6) protons. The *exo*-orientation of the H—C(6)—Br proton (δ 4.16) is indicated by the presence of rather large vicinal constant ($J_{1,6}$ = 4.8 Hz). The *endo*-protons of the H—C(2)—Br (δ 4.58) and H—C(5)—S (δ 4.02) groups show no interactions with the bridgehead protons but a W-coupling constant is observed, $J_{2,7}$ = 2.1 Hz and $J_{5,7'}$ = 2.6 Hz.

Compound **13** is a stereoisomer of compound **12** but the former is responsible for only four ^{1}H NMR signals, as it is highly symmetric. The structure containing *exo*-arylthio groups and *endo*-bromine atoms was chosen relying on calculations performed using the correlations proposed previously.[19,20]

Thus, the arenesulfenamide—phosphorus oxohalide system appears promising as a reagent for sulfenylation of dienes. The results of reactions with norbornadiene (**1**) attest that the reactions carried out in MeCN and CH_2Cl_2 involve different sulfenylating species.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 28 °C on a Varian VXR-400 instrument operating at 400 and 100 MHz, respectively, using $CDCl_3$ and CD_3CN as solvents. Nuclear Overhauser effect measurements were carried out in the difference spectroscopy mode (NOEDIF program). The melting points of substances were determined on a hot stage in an open capillary and were not corrected.

Arenesulfenamides were synthesized using a known procedure.[21] The formation of the monoamide dichloride of phosphorous acid (**11**) was confirmed by an alternative synthesis from $POCl_3$ and morpholine by a published procedure.[22] The course of the reaction was monitored by TLC on a fixed silica gel layer (Silufol).

Reactions of sulfenamides 2 with bicyclo[2.2.1]hepta-2,5-diene (1) in the presence of phosphorus(v) oxohalides in CH_2Cl_2 and AcOEt (general procedure). A solution of phosphorus(v) oxohalide (2 mmol) in the anhydrous solvent was slowly added with intense stirring at ~20 °C to a solution of sulfenamide **2** (2 mmol) in the same anhydrous solvent, and the mixture was stirred for 10 min. Then a solution of diene **1** (2 mmol) in the anhydrous solvent was slowly added, and the mixture was stirred until the reaction was over (1.5—4 h, TLC monitoring). The solvent was evaporated on a rotary evaporator and the residue was separated on a chromatographic column with SiO_2.

Reaction of sulfenamide 2b with bicyclo[2.2.1]hepta-2,5-diene (1) in the presence of $POCl_3$ in MeCN. A solution of $POCl_3$ (2 mmol) in the anhydrous solvent was slowly added with intense stirring at ~20 °C to a solution of sulfenamide **2b** (2 mmol) in the same solvent, and the mixture was stirred for 10 min. Then a solution of diene **1** (2 mmol) in the anhydrous solvent was slowly added, and the mixture was stirred until the reaction was over (2 h). The solvent was evaporated using a rotary evaporator and the residue was dissolved in $CHCl_3$, the solution was washed three times with water, and the washings were extracted with $CHCl_3$. The organic fraction was dried with Na_2SO_4, the solvent was evaporated, and the residue was separated on a chromatographic column with SiO_2.

Reaction of $POCl_3$-activated sulfenamide 2b with bicyclo[2.2.1]hepta-2,5-diene (1) in MeCN in the presence of $LiClO_4$. A solution of $POCl_3$ (2 mmol) in the anhydrous solvent and $LiClO_4$ (4 mmol) were slowly added with intense stirring at ~20 °C to a solution of sulfenamide **2b** (2 mmol) in the same solvent, and the mixture was stirred for 10 min. Then a solution of diene **1** (2 mmol) in the anhydrous solvent was slowly added, and the mixture was stirred until the reaction was over (TLC monitoring). The solvent was evaporated on a rotary evaporator, the residue was dissolved in $CHCl_3$, the solution was washed three times with water, and the washings were extracted with $CHCl_3$. The organic fraction was dried with Na_2SO_4, the $CHCl_3$ was evaporated, and the residue was separated on a chromatographic column with SiO_2.

Table 6. Chromatographic data and results of elemental analysis of the products of halosulfenylation of bicyclo[2.2.1]hepta-2,5-diene (**1**)

Compound	R_f (system)	Found / Calculated (%)			Molecular formula
		C	H	N	
4a	0.20	55.36 [b]	4.16 [b]	4.70 [b]	$C_{13}H_{12}ClNO_2S$
	($CHCl_3$—PE[a], 1 : 3)	55.42	4.26	4.97	
4b	0.54	54.83 [c]	4.39 [c]	4.72 [c]	$C_{13}H_{12}ClNO_2S$
	($CHCl_3$—PE, 1 : 1)	55.42	4.26	4.97	
4c	0.28	—	—	—	—
	(PE)				
4d	0.13	47.85 [d]	3.72 [d]	4.09 [d]	$C_{13}H_{12}BrNO_2S$
	($CHCl_3$—PE, 1 : 3)	47.85	3.68	4.29	
4e	0.19	47.60 [e]	3.97 [e]	4.06 [e]	$C_{13}H_{12}BrNO_2S$
	($CHCl_3$—PE, 1 : 3)	47.85	3.68	4.29	
4f	0.41	—	—	—	—
	(PE)				
5a	0.20	55.36 [b]	4.16 [b]	4.70 [b]	$C_{13}H_{12}ClNO_2S$
	($CHCl_3$—PE, 1 : 3)	55.42	4.26	4.97	
5b	0.54	54.83 [c]	4.39 [c]	4.72 [c]	$C_{13}H_{12}ClNO_2S$
	($CHCl_3$—PE, 1 : 1)	55.42	4.26	4.97	
5c	0.28	—	—	—	—
	(PE)				
5d	0.13	47.85 [d]	3.72 [d]	4.09 [d]	$C_{13}H_{12}BrNO_2S$
	($CHCl_3$—PE, 1 : 3)	47.85	3.68	4.29	
5e	0.19	47.60 [e]	3.97 [e]	4.06 [e]	$C_{13}H_{12}BrNO_2S$
	($CHCl_3$—PE, 1 : 3)	47.85	3.68	4.29	
5f	0.41	—	—	—	—
	(PE)				
6a	0.20	55.36 [b]	4.16 [b]	4.70 [b]	$C_{13}H_{12}ClNO_2S$
	($CHCl_3$—PE, 1 : 3)	55.42	4.26	4.97	
6b	0.54	54.83 [c]	4.39 [c]	4.72 [c]	$C_{13}H_{12}ClNO_2S$
	($CHCl_3$—PE, 1 : 1)	55.42	4.26	4.97	
6c	0.28	—	—	—	—
	(PE)				
6d	0.13	47.85 [d]	3.72 [d]	4.09 [d]	$C_{13}H_{12}BrNO_2S$
	($CHCl_3$—PE, 1 : 3)	47.85	3.68	4.29	
6e	0.18	—	—	—	—
	($CHCl_3$—PE, 1 : 3)				
6f	0.41	—	—	—	—
	(PE)				
7b	0.46	—	—	—	—
	($CHCl_3$—PE, 1:1)				
7c	0.28	—	—	—	—
	(PE)				
8	0.44	59.31 [f]	5.28 [f]	9.01 [f]	$C_{15}H_{16}N_2O_3S$
	($CHCl_3$)	59.21	5.26	9.21	
9	0.44	59.31 [f]	5.28 [f]	9.01 [f]	$C_{15}H_{16}N_2O_3S$
	($CHCl_3$)	59.21	5.26	9.21	

[a] PE is petroleum ether.
[b] For a mixture of isomers **4a**, **5a**, and **6a**.
[c] For a mixture of isomers **4b**, **5b**, and **6b**.
[d] For a mixture of isomers **4d**, **5d**, and **6d**.
[e] For a mixture of isomers **4e** and **5e**.
[f] For a mixture of isomers **8** and **9**.

The product yields are listed in Table 1, and the physicochemical characteristics of the products are given in Tables 3—6.

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