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Aminosulfenates in the Electrophilic Addition Reactions

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Abstract—The reactions of methyl and ethyl diethylaminosulfenates and ethyl piperidinylsulfenate with cyclohexene and norbornene in the presence of chloro- or bromotrimethysilanes were studied.

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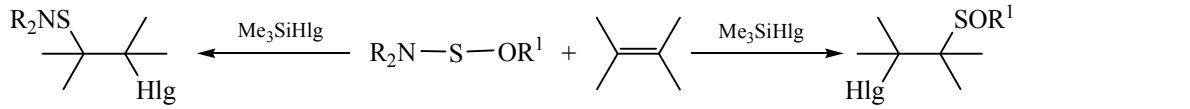
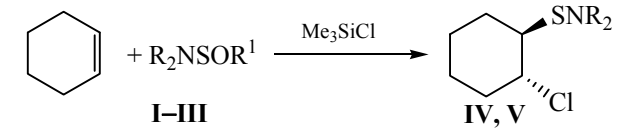
The reaction of ethylphenylsulfenate with alkenes in the presence of trimethylsilyl halides or trimethylsilyl isothiocyanate gives rise to β-halo-, β-thiocyanate- or β-isothiocyanate-substituted alkylphenylsulfides [1, 2].

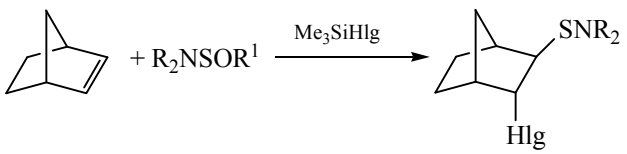
Continuing the studies of the electrophilic addition of sulfenic acid esters [1–3] to the unsaturated compounds, we examined the reactions of aminosulfenates (methyl diethylaminosulfenate **I**, ethyl diethylaminosulfenate **II**, ethyl piperidinylsulfenate **III**) with cyclohexene and norbornene in the presence of Me_3SiHlg (Hlg = Cl, Br). Owing to the presence of two basic atoms (nitrogen and oxygen) in the aminosulfenate molecule ($R_2N–S–OR'$), it is possible to predict two fundamentally different reaction pathways to form the corresponding amide or esters of sulfenic acid.



The reactions were found to proceed smoothly at room temperature to give the corresponding β-haloalkylsulfenamides in 40–90% yields (see the table), i. e., the coordination of a Lewis acid takes place via the oxygen atom.



I–III **IV, V**



I–III **VIa, VIb, VIIa, VIIb**

R = Et, R^1 = Me (**I**); R = Et, R^1 = Et (**II**); R_2 = $-(CH_2)_5-$, R^1 = Et (**III**); R = Et (**IV, VI**); R_2 = $-(CH_2)_5-$ (**V, VII**); Hlg = Cl (**VIa, VIIa**), Br (**VIb, VIIb**).

EXPERIMENTAL

The ^1H, ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ at 28°C relative to internal TMS. The mass spectra (EI, 70 eV) were registered on a Finnigan MIAT TSQ 7000 spectrometer. The reaction progress was monitored by TLC (Silufol UV254).

Compounds **I–III** were synthesized by the known procedure [4].

Reaction of aminosulfenates with alkenes in the presence of Me_3SiHlg (Hlg = Cl, Br). To a solution of 1.2 mmol of an alkene and 1.2 mmol of an aminosulfenate in 5 ml of anhydrous chloroform was slowly added under argon a solution of 1.2 mmol of trimethylsilyl halide in 5 ml of anhydrous chloroform with vigorous stirring at room temperature. The stirring was continued until the reaction completed.

The yields of the reaction products of aminosulfenates with alkenes in the presence of Me_3SiHlg (Hlg = Cl, Br)

Alkene	Aminosulfenate	Me_3SiHlg	Product	Yield,%
Cyclohexene	**I**	Me_3SiCl	**IV**	43
	II	Me_3SiCl	**IV**	37
	III	Me_3SiCl	**V**	32
Norbornene	**I**	Me_3SiCl	**VIa**	91
	I	Me_3SiBr	**VIb**	88
	II	Me_3SiCl	**VIa**	47
	II	Me_3SiBr	**VIb**	73
	III	Me_3SiCl	**VIIa**	42
	III	Me_3SiBr	**VIIb**	62

The reaction mixture was passed through a filter column (*h* 5 cm), the solvent was evaporated.

The yields of the obtained compounds are given in the table. The physicochemical characteristics of compound **VIIa** are identical to those published previously [5].

***trans*-(1-Chlorocyclohex-2-yl)sulfene *N,N*-diethylamide (IV).** R_f 0.78 (ethyl acetate:petroleum ether = 1:8). ^{1}H NMR spectrum, δ, ppm: 1.13 t (3H, CH_3, *J* 7.0 Hz), 1.35–1.45 m, 1.51–1.68 m, 1.71–1.82 m, 2.17–2.35 m (2H, CH), 2.93 q (4H, NCH_2, *J* 7.0 Hz), 4.20 t. d (1H, HCCl, *J* 6.6, *J* 3.9 Hz), the HCS proton is overlapped with the signals of NCH_2-proton. ^{13}C NMR spectrum, δ_C, ppm: 13.5 (CH_3), 22.8, 23.5, 28.5, 33.2, 52.6 [$N(CH_2)_2$], 54.3 (CS), 61.9 (CCl).

***trans*-(1-Chlorocyclohex-2-yl)sulfene piperidinide (V).** R_f 0.86 (ethyl acetate: petroleum ether = 1:8). ^{1}H NMR spectrum, δ, ppm: 1.41 m (2H, $CH_{2piperidine}$), 1.50–1.71 m (8H, $CH_{2cyclohexane}$, $CH_{2piperidine}$), 1.71–1.82 m, 216–2.34 m (2H, CH), 2.96 m (4H, NCH_2), 4.17 t. d (1H, HCCl, *J* 7.3, *J* 3.5 Hz), the HCS proton is overlapped with the signals of NCH_2-proton. ^{13}C NMR spectrum, δ_C, ppm: 22.5 ($CH_{2cyclohexane}$), 23.4 ($CH_{2piperidine}$), 24.1 ($CH_{2cyclohexane}$), 27.2 ($CH_{2piperidine}$), 29.8, 34.1 ($CH_{2cyclohexane}$), 53.5 (CS), 59.3 (NCH_2), 62.1 (CCl).

3-*endo*-Chlorobicyclo[2.2.1]hept-*exo*-2-yl)sulfene-diethylamide (VIa). R_f 0.57 (ethyl acetate:petroleum ether = 1:10). ^{1}H NMR spectrum, δ, ppm: 1.27 t (6H, CH_3, *J* 7.0 Hz), 1.39 d.d.t (1H, *anti*-H^7, $J_{7,7}$ 10.4, $J_{7,3}$ 2.7, *J* 2.0 Hz), 1.47 t.t.d (1H, *exo*-H^6, $J_{6,6} \sim J_{6,5exo}$ 12.5, $J_{6,5endo} \sim J_{6,1}$ 4.4, $J_{6,2}$ 2.0 Hz), 1.68 t. t (1H, *exo*-H^5, $J_{5,5} \sim J_{5,6exo}$ 12.2, $J_{5,6\ endo} \sim J_{5,4}$ 4.4 Hz), 1.69 d (1H, *syn*-H^7, $J_{7,7}$ 10.4 Hz), 1.99 d.d.d.d (1H, *endo*-H^6, $J_{6,6}$ 12.5, $J_{6,5endo}$ 9.2, $J_{6,5exo}$ 4.4, *J* 2.4 Hz), 2.27 d (1H, H^4, $J_{4,5exo}$ 4.4 Hz), 2.44 m (1H, H^1), 2.77 d.d (1H, HCS, $J_{3,2}$ 4.3, $J_{3,7}$ 2.7 Hz), 2.94 q (4H, NCH_2, *J* 7.0 Hz), 3.93 t. d (1H, HCCl, $J_{2,3}=J_{2,1}$ 4.3, $J_{2,6}$ 2.0 Hz). The signal of the *endo*-H^5 proton is overlapped with the signal of the *anti*-H^7 proton. ^{13}C NMR spectrum, δ_C, ppm: 13.7 (CH_3), 21.9 (C^6), 29.0 (C^5), 35.8 (C^7), 43.2 , 43.8 (C^1, C^4), 52.4 (NCH_2), 59.2 (CS), 65.8 (CCl). Found, %: C 56.30; H 8.43; N 5.86. $C_{11}H_{20}ClNS$. Calculated, %: C 56.51; H 8.56; N 5.99.

3-*endo*-Bromobicyclo[2.2.1]hept-*exo*-2-yl)sulfene-diethylamide (VIb). R_f 0.62 (ethyl acetate: petroleum ether = 1:8). ^{1}H NMR spectrum, δ, ppm: 1.17 t (6H, CH_3, *J* 7.0 Hz), 1.36 d.d.t (1H, *anti*-H^7, $J_{7,7}$ 10.4, $J_{7,3}$ 2.7, *J* 1.8 Hz), 1.53 t t.d (1H, *exo*-H^6, $J_{6,6} \sim J_{6,5exo}$ 12.2, $J_{6,5endo} \sim J_{6,1}$ 4.4, $J_{6,2}$ 2.0 Hz), 1.66 t. t (1H, *exo*-H^5, $J_{5,5} \sim J_{5,6exo}$ 12.2, $J_{5,6endo} \sim J_{5,4}$ 4.4 Hz), 1.68 d (1H, *syn*-H^7, $J_{7,7}$ 10.4 Hz), 1.97 d.d.d.d (1H, *endo*-H^6, $J_{6,6}$ 12.4, $J_{6,5endo}$ 9.0, $J_{6,5exo}$ 4.2, *J* 2.3 Hz), 2.23 d (1H, H^4, $J_{4,5exo}$ 4.4 Hz), 2.46 m (1H, H^1), 2.88 d. d (1H, HCS, $J_{3,2}$ 4.3, $J_{3,7}$ 2.7 Hz), 2.93 q (4H, NCH_2, *J* 7.0 Hz), 3.96 t.d (1H, HCBr, $J_{2,3}=J_{2,1}$ 4.4, $J_{2,6}$ 2.0 Hz). The signal of the *endo*-H^5 proton is overlapped with the signal of the *anti*-H^7 proton. ^{13}C NMR spectrum, δ_C, ppm: 13.7 (CH_3), 24.1 (C^6), 28.9 (C^5), 35.4 (C^7), 43.2 , 44.1 (C^1 и C^4), 52.5 (NCH_2), 58.0 (CS), 59.6 (CBr). Mass spectrum, *m*/*z* (I_{rel}, %): 279 (45), 277 (45) $[M]^+$, 185 (13), 183 (13), 175 (17), 173 (17), 105 (100), 104 (57), 93 (62), 91 (21), 90 (52). Found, %: C 47.30; H 7.12; N 5.19. $C_{11}H_{20}BrNS$. Calculated, %: C 47.48; H 7.19; N 5.04. *M* 278.25

3-*endo*-Bromobicyclo[2.2.1]hept-*exo*-2-yl)sulfene-piperidinide (VIIb). R_f 0.72 (ethyl acetate:petroleum ether = 1:10). ^{1}H NMR spectrum, δ, ppm: 1.33–1.43 m (4H, *endo*-H^5, *anti*-H^7, $CH_{2piperidine}$), 1.44–1.70 m (7H, *exo*-H^5, *exo*-H^6, *syn*-H^7, $CH_{2piperidine}$), 1.60 m (4H, $CH_{2piperidine}$), 1.98 d.d.d.d (1H, *endo*-H^6, $J_{6,6}$ 12.4, $J_{6,5endo}$ 8.9, $J_{6,5exo}$ 4.2, *J* 2.4 Hz), 2.19 d (1H, H^4, *J* 4.4 Hz), 2.46 m (1H, H^1), 3.00 m (4H, H_2CN), 4.02 t.d (1H, HCBr, *J* 4.4, *J* 2.0 Hz). The signal of the HCS proton is overlapped with the signal of the NCH_2 protons. ^{13}C NMR spectrum, δ_C, ppm: 23.2 ($CH_{2piperidine}$), 24.1 (C^6), 27.3 ($CH_{2piperidine}$), 29.0 (C^5), 35.6 (C^7), 43.7, 44.1 (C^1 and C^4), 58.7 (NCH_2), 57.6 (CS), 59.4 (CBr). Mass spectrum, *m*/*z* (I_{rel}, %): 291 (31), 289 (31) $[M]^+$, 197 (10), 195 (10), 175 (9), 173 (9), 117 (100), 93 (28), 85 (27). *M* 290.26.

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REFERENCES

1. Zyk, N.V., Gavrilova, A.Yu., Mukhina, O.A., Bondarenko, O.B., and Zefirov, N.S., *Russ. Chem. Bull., Int. Ed.,* 2008, vol. 57, no. 12, p. 2572.
2. Zyk, N.V., Gavrilova, A.Yu., Mukhina, O.A., Borisenko, A.A., Bondarenko, O.B., and Zefirov, N.S., *Izv. Russ. Chem. Bull., Int. Ed.,* 2010, vol. 59, no. 9, p. 1771.
3. Zyk, N.V., Gavrilova, A.Yu., Mukhina, O.A., Bondarenko, O.B., and Zefirov, N.S., *Russ. J. Org. Chem.,* 2006, vol. 42, no. 12, p. 1856.
4. Almazi, L. and Hanta, A., *Chem. Ber*., 1966, vol. 99, p. 3288.
5. Zyk, N.V., Gavrilova, A.Yu., Nechaev, M.A., Bondarenko, O.B., and Zefirov, N.S., *Russ. Chem. Bull., Int. Ed.,* 2009, vol. 58, no. 12, p. 2517.