ISSN 0965-5441, Petroleum Chemistry, 2009, Vol. 49, No. 3, pp. 254–260. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © S.A. Mamedov, F.A. Fatali-zade, N.P. Ladokhina, M.F. Farzaliev, M.E. Musaeva, 2009, published in Neftekhimiya, 2009, Vol. 49, No. 3, pp. 272–277.

Synthesis and Transformations of Aziridinesulfonamide Derivatives and Their Investigation as Lubricant Additives

S. A. Mamedov, F. A. Fatali-zade, N. P. Ladokhina, M. F. Farzaliev, and M. E. Musaeva

Institute of Chemistry of Additives, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan

e-mail: nina_fuad@rambler.ru

Received April 08, 2008

Abstract—The methods for the synthesis of aziridinesulfonamide derivatives by chlorine substitution in *N*-β-chloroalkylsulfonamides were developed. It was found that the chlorine atom in the 3-position of aziridinesulfonamides is more reactive than that in the 4-position. It was found that the reactions of 3- and 4-chloroalkylaziridinesulfonamides with amylmercaptan in the presence of alkali lead to the replacement of the chlorine atom with the hydroxyl group along with the opening of the aziridine cycle. The reaction of 4-chloroalkylaziridinesulfonamides with 2 moles of amylmercaptan results in both chlorine substitution and aziridine cycle opening. The investigation of the synthesized compounds as additives for lubricants showed their high anticorrosive, antioxidant, and antiwear efficiency.

DOI: 10.1134/S0965544109030128

Previously [1], we have investigated conditions for the synthesis of β-chloroalkylarenelsulfonamides via the reaction of *N*-β-chlorosulfonamides with α-olefins. The reactivity of chlorine in the *N*-β position towards various nucleophiles has been investigated. Among *N*-β-chloroalkylarenesulfonamide derivatives, their aziridine derivatives are of particular interest. These compounds are widely used for the synthesis of aminopyrroles [2, 3] and imidazoles [4, 5].

The aziridine cycle is easily opened even by potassium thiocyanate to form thiazolidines [6, 7], which demonstrates its high reactivity.

The synthesis of aziridinesulfonamides is usually carried out by the reaction of sulfonyl chlorides with ethyleneimine at 30–35°C in the presence of a base [8]. However, the most practical reagents for the synthesis of aziridinesulfonamides are *N*-β-chlorosubstituted sulfonamides (*1*–*3*) previously described in [1].

EXPERIMENTAL

All NMR spectra were recorded on Varian and Tesla spectrometers operating at 60 and 90 MHz in CCL_4, or CF_3COOH solutions with HMDS as an internal standard. IR spectra were recorded on UR-20 and Specord 75 IR spectrometers. The physicochemical characteristics of the compounds are given in Table 1.

The synthesized compounds were examined as additives according to standard procedures.

*2-Alkyl(or 2-chloroalkyl, or 3-chloroalkyl)-N-(4-chlorobenzenesulfonyl)aziridines (**4–6**)*

General procedure. To a solution of 0.5 mol of *N*-(2-chlorohexyl)-4-chlorobenzenesulfonamide (*1*), or *N*-(1,5-dichloro-2-nonyl)-4-chlorobenzenesulfonamide (*2*), or *N*-(2,4-dichlorononyl)-4-chlorobenzenesulfonamide (*3*) in 200–250 ml of benzene, 190 ml of 10% aqueous NaOH solution was added at 10–20°C. The mixture was stirred at 20°C for 60 min. The benzene layer was separated, washed with water until neutral reaction, and dried. Benzene was distilled off, and the residue was distilled under a vacuum.

*2-(3-Hydroxyheptyl)-N-(4-chlorobenzenesulfonyl)aziridine (**7**)*

To a solution of 38.6 g (0.1 mol) of *N*-(1,5-dichloro-2-nonyl)-4-chlorobenzenesulfonamide (*2*) in 100 ml of benzene, 32 ml of 20% NaOH aqueous solution was added at 30–32°C. The mixture was left to stay overnight; then, the benzene layer was separated, washed with water, and dried. Benzene was distilled off, and the residue was distilled under a vacuum.

*2-(4-Hydroxyheptyl)-N-(4-chlorobenzenesulfonyl)aziridine (**8**)*

To a solution of 38.6 g (0.1 mol) of *N*-(2,4-dichlorononyl)-4-chlorobenzenesulfonamide (*3*) in 100 ml of benzene, 32 ml of 20% NaOH aqueous solution was added. The mixture was refluxed at 78–80°C for 60 min. After cooling, the benzene layer was separated and dried. Benzene was distilled off, and the residue was distilled under a vacuum.

Table 1. Physicochemical characteristics of compounds ***4–13***

Compound no.	Yield, %	T_{bp}, °C (mmHg)	d_4^{20}	n_D^{20}	Found/calculated, %		
					C	H	H
4	88.5	65–66/0.4	1.0788	1.4719	52.69/52.46	5.98/5.86	5.42/5.09
5	80.2	130–132/0.1	1.2159	1.5332	51.80/51.27	6.55/6.02	3.80/3.99
6	76.4	142–143/0.4	1.2183	1.5340	51.60/51.27	6.35/6.02	3.66/3.99
7	74.9	142–143/0.1	1.2219	1.5380	54.55/54.29	6.92/6.68	4.22/4.22
8	81.8	161–163/0.2	1.2259	1.5399	54.41/54.29	6.92/6.68	4.48/4.22
9	78.9	174–175/0.3	1.1766	1.5266	60.88/60.58	7.67/7.34	4.17/3.92
10	76.8	198–199/0.45	1.0834	1.5238	55.45/55.09	8.14/7.85	3.48/3.21
11	72.6	200–202/0.4	1.1340	1.5267	55.41/55.09	8.11/7.85	3.52/3.21
12	75.0	215–216/0.55	1.1729	1.5300	53.85/53.59	7.62/7.25	3.19/2.84
13	77.9	193–194/0.4	1.1150	1.5288	57.87/57.49	8.83/8.49	2.98/2.68

*2-(3-Oxyallylheptyl)-N-(4-chlorobenzenesulfonyl)aziridine (**9**)*

To a mixture of 5.6 g (5.5 mmol) of triethylamine and 2.9 g (50 mmol) of allyl alcohol, a solution of 16.6 g (50 mmol) of 2-(3-chloroheptyl)-*N*-(4-chlorobenzenesulfonyl)aziridine (6) in 50 ml of benzene was added dropwise at 20–30°C. The mixture was heated at 50–60°C for 1–2 h, cooled, and filtered. The resulted benzene solution was washed with water and dried. Benzene was distilled off, and the residue was distilled under a vacuum.

*2-(4-Chlorobenzenesulfonamido)-1-amylthio-5-hydroxynonane (**10**)*

To a solution of 1.6 g (40 mmol) of NaOH in 6 ml of water, 4.16 g (40 mmol) of amylmercaptan was added. Then, a solution of 15.4 g (40 mmol) of 2-(4-chloroheptyl)-*N*-(4-chlorobenzenesulfonyl)aziridine (*5*) in 50 ml of benzene was added dropwise at 50°C. The mixture was refluxed for 2.5–3 h, the benzene layer was separated, washed with water, and dried. Benzene was distilled off, and the residue was distilled under a vacuum.

In a similar way, 2-(4-chlorobenzenesulfonamido)-1-amylthio-4-hydroxynonane (***11***) was prepared from 2-(3-chloroheptyl)-*N*-(4-chlorobenzenesulfonyl)aziridine (*6*).

*2-(4-Chlorobenzenesulfonamido)-1-amylthio-5-(carboxymethyloxy)nonane (**12**)*

To a solution of 8.2 g (20 mmol) of 2-(4-chlorobenzenesulfonamido)-1-amylthio-4-hydroxynonane (*11*) in 20 ml of benzene, 2.5 g (2.5 mmol) of triethylamine was added. Then, a solution of 2.36 g of chloroacetic acid in 20 ml of ethanol was added and the mixture was refluxed for 2–3 h. After the addition of 50 ml of water, the benzene layer was separated and dried. Benzene

was distilled off, and the residue was distilled under a vacuum.

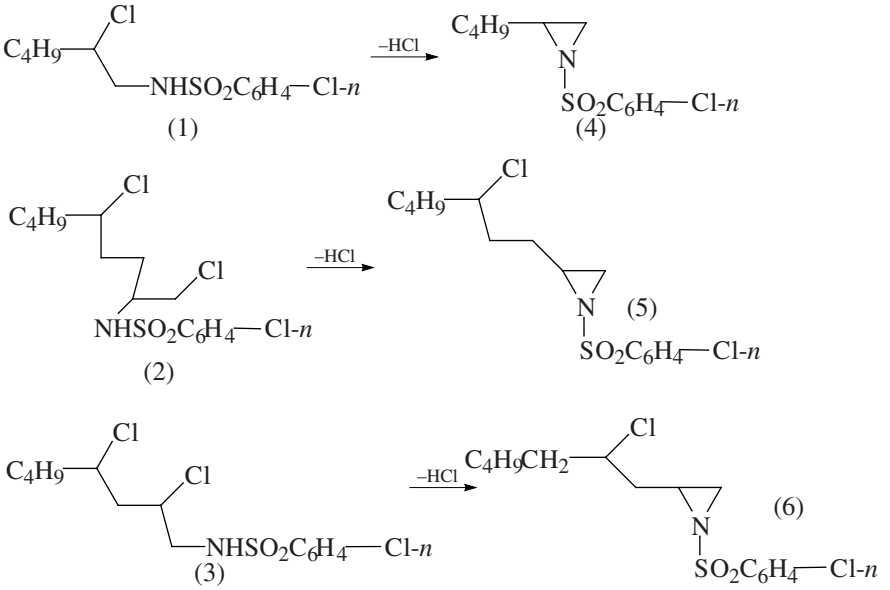
*2-(4-Chlorobenzenesulfonamido)-1,5-bis(amylthio)nonane (**13**)*

To a solution of 4 g (100 mmol) of NaOH in 50 ml of ethanol, 20.8 g (200 mmol) of amylmercaptan was added. Then, a solution of 34.6 g (100 mmol) of 2-(4-chloroheptyl)-*N*-(4-chlorobenzenesulfonyl)aziridine (*5*) in 50 ml of ethanol was added dropwise at 40–50°C. The mixture was heated at 50–60°C for 2.5–3 h, ethanol was distilled off, and 100 ml of benzene was added. The benzene layer was separated, washed with water, and dried. Benzene was distilled off, and the residue was distilled under a vacuum.

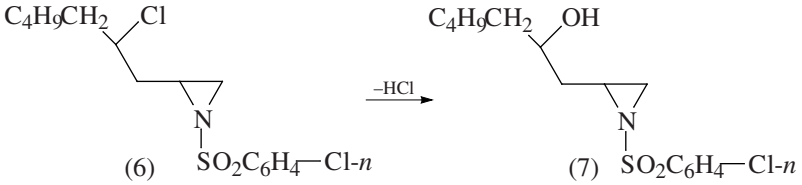
The structures of compounds *10, 11*, and *13* were confirmed by their ^{1}H NMR spectra.

RESULTS AND DISCUSSION

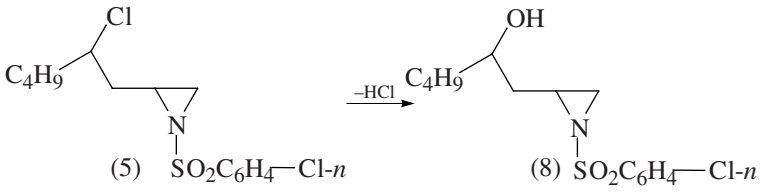
Because of the electrophilic character of the sulfonamide group, the treatment of *N*-(β-chloroalkyl)arenesulfonamides with potassium alcoholate or a KOH ethanolic solution, even in the cold, results in the elimination of hydrogen chloride to give aziridine derivatives. Further investigations have shown that hydrogen chloride elimination is caused even by treatment with a 10% alkali aqueous solution at room temperature.



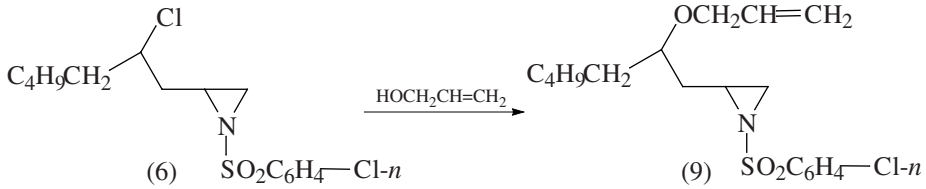
In the case of concentrated alkali solution or long-term storage in a dilute solution, the second chlorine atom in product *6* is readily replaced with the hydroxyl group owing to the inductive effect of the sulfonamide group.



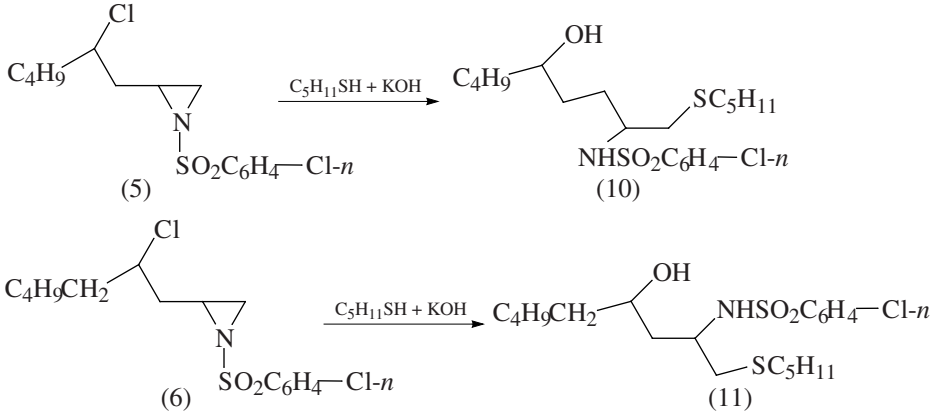
However, the hydrolytic substitution chlorine in product *5* proceeds at higher temperatures (80–90°C) or with the use of a more concentrated alkali solution.



The substitution of other nucleophilic agents for chlorine in products *5* and *6* also proceeds easily. Depending on the reagents and reaction conditions, the opening of the aziridine ring can take place along with the chlorine substitution reaction, in agreement with published data. It has been shown [9, 10] that the aziridine cycle in sulfonamides is easy to open by nucleophiles. However, we revealed that the aziridine cycle opening reaction depends on the nature of the nucleophile. For example, the reaction of *6* with allyl alcohol under mild conditions in the presence of triethylamine or pyridine leads only to chlorine substitution with the obtainment of ether *9*.



In the reaction of *5* and *6* with amylmercaptan in the presence of alkali, the substitution of the chlorine atom by the hydroxyl group occurs along with the opening of the aziridine cycle.



The presence of hydroxyl in compounds *10* and *11* was proven by ^{1}H NMR spectroscopy, as well as by the transformation of *10* into the ester by its reaction with chloroacetic acid.

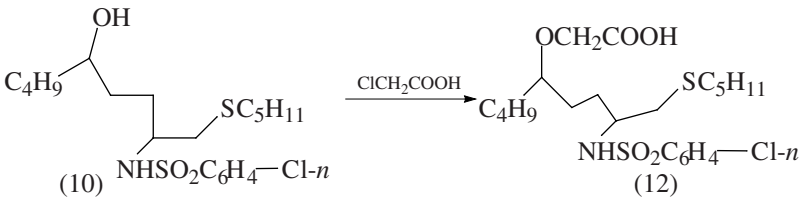
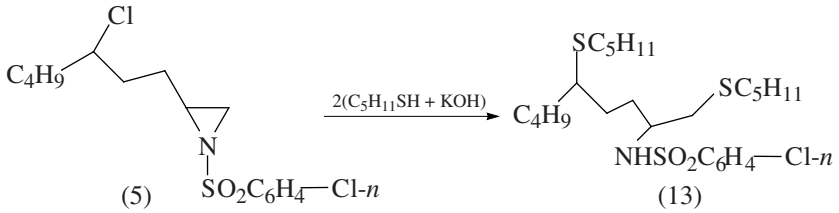


Table 2. Results of testing compounds ***4–13*** as additives for M-11 oil

Compound no.	Content of additives in 100 g of M-11 oil		Corrosion, g/m^2	Antiwear and extreme pressure characteristics, 392 N, 1 h		Thermooxidative stability by a DK NAMI test	
	mmol	g		WSD, mm	LWI	Deposit, %	Viscosity increment
1	2	3	4	5	6	7	8
4	3	0.82	120.1	0.78	–	12.9	22.1
	5	1.37	97.9	0.71	–	12.8	29.9
	10	2.74	33.5	0.64	–	4.0	16.7
5	3	1.05	61.3	0.73	34	7.66	21.1
	5	1.75	38.7	0.67	9	4.8	19.8
	10	3.5	16.1	0.50	46	2.0	10.4
6	3	1.05	51.2	0.52	36	6.4	12.5
	5	1.75	30.1	0.46	40	3.7	9.8
	10	3.5	8.1	0.41	48	1.4	8.9
8	3	1.0	32.5	0.75	–	4.1	11.2
	5	1.66	26.8	0.69	–	3.3	8.5
	10	3.32	10.9	0.62	–	1.73	7.3
9	3	1.12	48.7	0.52	47	6.0	13.9
	5	1.86	34.6	0.48	50	4.3	9.8
	10	3.72	10.1	0.42	54	1.1	8.7
12	3	1.48	5.89	0.48	45	1.6	8.9
	5	2.47	2.30	0.40	59	0.6	7.0
	10	4.94	1.10	0.38	68	0.25	6.1
13	3	1.56	6.91	0.50	47	1.65	8.6
	5	2.13	4.2	0.40	59	0.81	7.1
	10	5.22	1.4	0.38	70	0.30	6.4
DF-11*	–	1	24.7	0.63	–	–	–
	–	2	4.0	0.40	–	–	–
VNIINP-300*	–	2.4	3.9	–	–	–	–
IKhP-21*	–	2	5.1	–		13.27	65.4
	–	4	2.2	0.61		10.46	78.1
Ionol*	–	1.0	–			2.6	75.4

By treatment of *5* with two moles of amylmercaptan at 50–60°C, the chlorine substitution and aziridine ring opening reactions proceed simultaneously.



(5) (13)

The analogous reaction of *6* leads to product *11*, regardless of the reaction conditions.

Analysis of the published data shows that, despite a wide variety of sulfonamide compounds, they have been investigated as lubricant additives to a lesser extent compared to other application areas. A large group of sulfanilides [11–15] has been investigated as antioxidant, detergent, corrosion-inhibiting, antiwear, and extreme-pressure additives for lubricants. Taking this into account, we have comprehensively investigated anticorrosive, antiwear, extreme-pressure, and antioxidant characteristics of the synthesized compounds *4–13*.

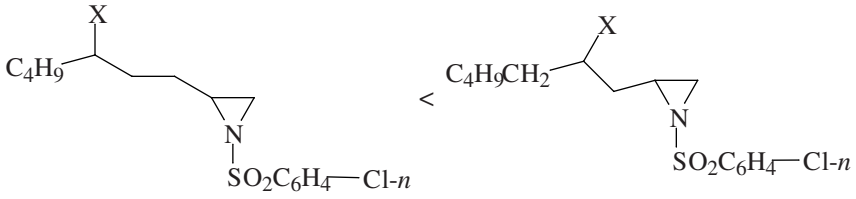
The results of testing the properties of the synthesized compounds in comparison with the industrial additives are represented in Table 2. As can be seen, there are very effective additives among the compounds prepared. Their performance depends on their structure and composition. The aziridine moiety has an unfavorable effect on the corrosion-inhibiting properties of the compounds. The presence of a long-chain alkyl radical (compounds *5* and *6*) enhances the anticorrosive efficiency. The replacement of chlorine with the hydroxyl (compound *7*) or the allyl (compound *9*) group does not influence the anticorrosive characteristics of the compounds. However, the compounds prepared via reactions involving aziridine cycle opening (compounds *9, 12*, and *13*) display a very high anticorrosive activity.

The investigation into the influence of the concentration of aziridinesulfonamides and their derivatives on the corrosion-inhibiting properties of oils has shown that the optimal concentration for preventing corrosion (5 g/m^2) in the M-11 oil is 10 mmol and even lower (3–5 mmol) for compounds *12* and *13*.

The study of the effect of aziridinesulfonamides and their derivatives on the extreme-pressure characteristics has shown that the aziridine moiety worsens the extreme-pressure properties, although they are superior to the initial chlorinated sulfonamides *1–3* in antiwear characteristics. Aziridine *6* is more effective than *4*. In addition, the replacement of chlorine in aziridine *4* with the hydroxyl group (compound *7*) worsens and the presence of the allyl group (compound *9*) improves the antiwear and extreme-pressure characteristics. In contrast to aziridines *4–6*, their transformation products *9, 12*, and *13* exhibit a high antiwear and extreme-pressure efficiency.

The study of the influence of the concentration of compounds *4–13* on the antiwear characteristics of the M-11 oil has shown that the optimal concentration providing a minimum wear scar diameter is 10 mmol per 100 g of oil for compounds *4–6* and is even lower (5 mmol) for compounds *9, 12*, and *13*. The antiwear efficiency of the latter compounds, even at a 5 mmol concentration, is about 1.5–2 times that of other derivatives. Regarding the concentration effect of these compounds on oil M-11 extreme pressure characteristics, it should be pointed out that their efficiency is highly dependent on concentration. Compounds *12* and *13* are more effective than the other compounds, even at concentrations of 5 mmol per 100 g of oil.

Testing the aziridinesulfonamides and their transformation products has shown their high antioxidant efficiency. The compounds containing the chlorine atom and a functional group in the 1,3-positions are more efficient than those containing the substituents in the 1,4-positions, because of the interplay with the sulfonamide group.



Compounds *12* and *13* containing the thioether and ether groups proved to be highly effective antioxidant additives. In their performance, they are superior to some extent to other sulfonamide derivatives, as well as certain industrial additives.

REFERENCES

1. S. A. Mamedov, A. M. Levshina, K. O. Kerimov, et al., Neftekhimiya **28**, 396 (1988).
2. W. Klotzer, Monatsh. Chem. **101**, 1841 (1970).
3. A. Laurent, P. Mison, A. Nafti, and N. Pellisier, Tetrahedron Lett., No. 46, 4511.
4. B. Again, G. Hornyak, K. Lemperi, and G. Simig, Chem. Eng. Sci. **26**, 211 (1982).
5. G. Simig and P. Szepesy, Chem. Eng. Sci. **20**, 241 (1976).
6. R. D. Westland, M. H. Lin, and J. M. Vandenbel, J. Heterocycl. Chem. **8**, 405 (1971).
7. M. Weitzberq, Z. Aizenshtat, and J. Blum, J. Heterocycl. Chem. **21**, 1597 (1984).
8. H. Martin and C. S. Sprague, US Patent No. 3,431,152 (1968).
9. S. Ljunggren, K. J. Hoffman, R. Stenberq, et al., J. Med. Chem. **17**, 649 (1974).
10. I. Irikura, S. Sudzue, I. Khasachava, and Kh. Kavasaki, JP Appl. No. 49-21137 (1974).
11. G. G. Moore and E. S. Rothman, US Patent No. 3,567,74 (1971).
12. S. Schiff, US Patent No. 3,766,150 (1973).
13. K. J. Chou, US Patent No. 4,194,982 (1980).
14. A. Abdul-Malek, C. G. Bransen, and W. S. Edmiston, US Patent No. 4,149,980 (1979).
15. E. B. Sushko, P. S. Belov, and V. A. Trofimov, Khim. Tekhnol. Topl. Masel, No. 5, 36 (1983).
16. V. E. Bukin and P. G. Chernichenko, UA Patent No. 44571 (2002).