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Synthesis of *N*-Substituted Derivatives of Arylsulfonyl Hydrazides and Their Investigation as Additives for Lubricating Oils

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Abstract—The reaction between arylsulfonyl chlorides and hydrazine has been studied, and it has been found that in the presence of excess hydrazine, the bis-derivatives are produced in small amounts along with monoarylsulfonyl hydrazides. It has been revealed that the reaction of monosulfonyl hydrazides with alkyl bromides in the presence of a base results only in *N*-alkylation of the sulfamide nitrogen, although the reaction in the presence of HCl proceeds at the amine group with the formation of quaternary ammonium salts. A method for the preparation of sulfonyl hydrazides by oxidation of *N*-alkyl sulfamides in the presence of iodine has been developed. Some arylsulfonyl hydrazide derivatives have been examined as antioxidant, antirust, and antiwear additives. These sulfonyl hydrazides also exhibit a high bactericidal and fungicidal activity.

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The products of the reaction of arylsulfonyl chlorides with polyamines are being currently studied as additives for lubricating oils and greases. It is also known that they exhibit antiarrhythmic, antitumor, and antibacterial activities [1–3].

EXPERIMENTAL

Procedures for the synthesis of various arylsulfonyl hydrazides are described below.

Arylsulfonyl hydrazides (compounds 1–3) Hydrazine sulfate in an amount of 0.1 mol was added to 0.05 mol of arylsulfonyl chloride and the resultant mixture was diluted with water at 20°C. Afterwards, the reaction was initiated by adding drop wise 0.2 mol of 30% NaOH solution until pH 7.3. During the addition of the alkali, the temperature of the medium increased to 25–35°C and was maintained at this level for 2–2.5 h. Then the temperature was slowly elevated to 90°C and maintained for 9 h. The precipitate formed was washed with water to neutral reaction, and the resulting crystals were dissolved in benzene. The benzene solution was filtered and concentrated by evaporation. Isooctane was added to the concentrated solution, and arylsulfonyl hydrazides 1–3 were isolated.

The products insoluble in benzene were recrystallized from ethanol. A study of their structure and composition showed them to be *N,N'*-bisarylsulfonyl hydrazides.

***N*-Alkyl-*N*-4-methylpenylsulfonyl hydrazides** (compounds 4, 5) A mixture contained 0.05 mol of 4-methylpenylsulfonyl hydrazide 1 and 0.1 mol of 20% aqueous NaOH solution was vigorously stirred for 30 min at 90–98°C. Afterwards, 0.06 mol of *n*-butyl or *n*-octyl bromide was added dropwise to the reaction mixture at this temperature, and the resulting mixture was additionally stirred for 3 h and then cooled. The obtained crystals were filtered off, washed with water, and recrystallized from an ethanol–benzene blend (2 : 1).

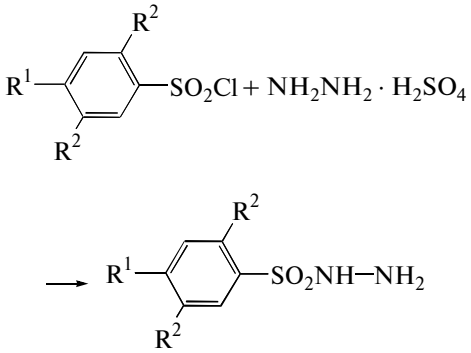
Quaternary salts of arylsulfonyl hydrazides (compounds 6–8). Arylsulfonyl hydrazide 1–3 (0.1 mol) was dissolved in a mixture of diethyl ether and benzene (1 : 1), and hydrogen chloride was bubbled through the resulting mixture until complete precipitation of crystals. The obtained crystals were filtered off and recrystallized from ethanol. The crystals were hydroscopic (deliquescent plates).

***N,N'*-Dialkyl-*N,N'*-bis(arylsulfonyl hydrazides)** (compounds 9–11). The corresponding *N*-alkyl-*N*-arylsulfonyl hydrazide (0.1 mol) was mixed with 0.12 mol of 30% aqueous NaOH solution and heated until its complete dissolution. Then, 0.2 mol of crystalline iodine was added to the reaction mixture; the mixture was heated for 2 h, and 10 mL of diluted HCl (1 : 1) was added. If the resultant medium was colored, it was treated with 0.1 N sodium sulfite solution till disappearance of the color. The obtained crystals were filtered off with a sintered-glass funnel, washed with water, and recrystallized from ethanol.

Analysis methods. The ^{1}H NMR spectra the synthesized compounds were recorded on a Varian T-60 and Tesla-467 spectrometers operating at frequencies of 60 and 90 MHz.

RESULTS AND DISCUSSION

The available published data on the reaction of arylsulfonyl chloride with hydrazines are controversial. For example, it was shown that the reaction between arylsulfonyl chloride and hydrazine results in the formation of monosulfonyl hydrazides [4] of disulfonyl hydrazides when the reactants are used in the 1 : 1 or 2 : 1 molar ratio, respectively . However, we have shown that the reaction in the presence of excess hydrazine yields bis-arylsulfonyl hydrazides along with monoarylsulfonyl hydrazides (see the scheme below):

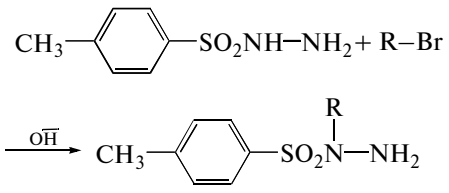


(1–3)

$R^1 = CH_3$, $R^2 = H$ (1); $R^1 = H$, $R^2 = CH_3$ (2);
$R^1 = Br$, $R^2 = H$ (3).

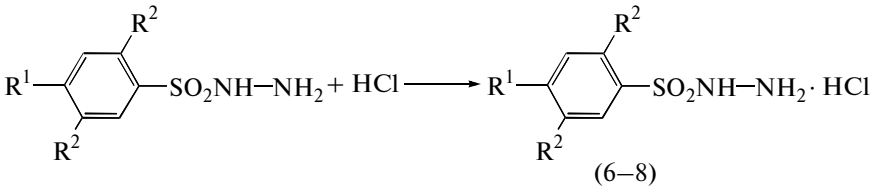
Despite the excess of hydrazine, the yield of arylsulfonyl hydrazides does not exceed 30–32% and depends on the nature of arylsulfonyl chloride. Thus, the yields of sulfonyl hydrazides obtained by the reaction of 4-methylphenyl, 4-bromophenyl, and 2,5-dimethylphenyl sulfonyl chlorides with hydrazine are 16.5, 18.5, and 31%, respectively, thereby providing evidence for the effect of the substituent nature.

The reaction of 4-methylphenylsulfonyl hydrazide with alkyl bromides in the presence of the base resulted in the formation of *N*-alkyl derivatives of sulfonyl hydrazides. The spectral data confirmed the fact of *N*-alkylation of the sulfamide nitrogen via the following reaction:



$R = C_4H_9$ (4); C_8H_{17} (5)

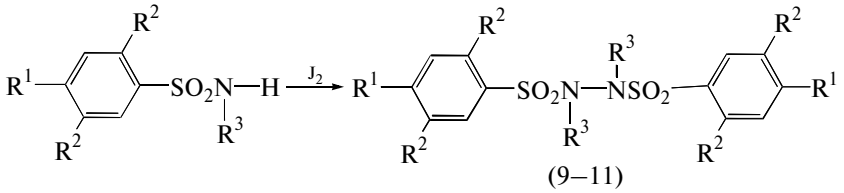
The reaction of arylsulfonyl hydrazides **1–3** with hydrogen chloride gives the quaternary ammonium salts:



(6–8)

$R^1 = CH_3$, $R^2 = H$ (6); $R^1 = H$, $R^2 = CH_3$ (7);
$R^1 = Br$, $R^2 = H$ (8).

To compare and study the influence of the alkylradical on the hydrazine nitrogen atoms on the performance characteristics, we synthesized a series of *N*,*N*'-dialkyl-*N*,*N*'-bis(arylsulfonyl hydrazide)s by oxidation of *N*-alkyl-*N*-arylsulfamides:



(9–11)

$R^1 = H$, $R^2 = H$; $R^3 = C_2H_5$ (9); $R^1 = H$, $R^2 = CH_3$,
$R^3 = C_2H_5$ (10); $R^1 = CH_3$, $R^2 = H$, $R^3 = C_4H_9$ (11).

Arylsulfonyl hydrazides are synthons in synthesis of various heterocyclic compounds that have promise as bactericides [5].

Table 1. Results of testing arylsulfonyl hydrazides as additives for lubricating oils and greases

Compound no.	Additive content in oil or grease	Induction period for sludge formation, precipitate, %	Corrosion, g/m^2	Antiwear properties at load of 392 N	
				d, mm	A_p
Oil M-8	–	0	160	–	–
AK-15	–	–	–	0.68	20.1
4	3	0.75	21.2	0.60	56
5	1	0.09	13.8	0.55	60
	3	0.15	6.1	0.50	66
9	1	2.5	30.5	0.60	46
	3	1.1	19.8	0.51	56
11	3	1.2	20.7	0.55	52
	5	0.8	14.5	0.50	66
DF-11	2	–	4.0	0.48	68
VNIINP-300	2.4	–	3.9	0.61	62
Grease 141/l	–	–	58.9	0.59	48
Compound 5	3	–	5.6	0.51	68
Compound 11	3	–	6.2	0.50	67

Our preliminary studies showed [6, 7] that compounds containing simultaneously the sulfamide group together with other functional groups and heterocyclic moieties exhibit good antirust, antioxidant, and tribological properties as components of lubricating oils. To improve these properties of lubricating greases, sulfamide compounds were also used [8, 9]. In light of this information, the arylsulfonyl hydrazides synthesized in the present study that are soluble in the M-8 and AK-15 oils were screened as additives for lubricating oils and greases.

The oil solubility of compounds 1–3 does not exceed 2%; therefore, they were not tested as lubricating oil additives. Well-soluble compounds 4, 5, 9, 11 displayed high antioxidant and antiwear properties (Table 1).

Sulfonyl hydrazides 4, 5, 9, 11 were also studied as antirust and antiwear additives in lubricating grease compositions obtained previously [10, 11]. From the data Table 1 it follows that a 3% concentration of compound 5 or 11 sharply reduces the corrosiveness and enhances the tribological properties of the oil; and they decrease the corrosion in the 141/L sealing grease from 58.9 to 5.6 g/m^2 (the absence of corrosion). These compounds can be used as antirust and antiwear additives for greases.

Note that in contrast to the known methods, these sulfamide compounds were added to the grease during its preparation at130–140°C.

Synthesized arylsulfonyl hydrazides were also studied as antimicrobial additives in the M-8 oil (compds. 4, 5, 11) and in the Azerol cutting fluid (compds. 9, 10). Bactericidal activity of the synthesized compounds was determined according to GOST 9.052-88 using the following microorganisms: a mixture of fungi (*Aspergillus niger*, *Penicillium chrysogenum*, *Penicil-*

Table 2. Results of testing arylsulfonyl hydrazides 4–7and 11 as antimicrobial additives to lubricating oils and cutting fluids

M-8 oil or cutting fluid	Compound no	Concentration, %	Diameter of microorganism suppression zone, cm	
			Bacterial mixture	Fungi mixture
M-8 oil	4	1	2.6	3.2
		0.5	2.3	2.4
		0.25	1.8	2.0
		0.1	1.4	1.8
M-8 oil	5	1	2.8	3.5
		0.5	2.5	2.8
		0.25	2.0	2.5
		0.1	1.8	2.0
M-8 oil	11	1	3.4	3.8
		0.5	3.0	3.5
		0.25	3.0	2.8
		0.1	2.4	2.6
Cutting fluid Azerol	6	1	3.8	3.2
		0.5	3.6	3.0
		0.25	3.2	2.8
		0.1	2.8	2.3
Cutting fluid Azerol	7	1	3.7	3.4
		0.5	3.5	3.0
		0.25	2.8	2.6
		0.1	2.4	2.2
Sulfoxide		1	1.9	3.4
		0.5	1.4	2.4
		0.25	1.2	2.0
		0.1	1.0	1.4

lium cyclopium, *Paccilomuges varioti*, *Scopulariopsis brevicaulis*) and a mixture of bacteria (*Pseudomonas aeruginosa*, *Mycobacterum*).

As follows from the data in Table 2, *N*-alkyl substituted derivatives of monosulfonyl hydrazides 4, 5 and *N*,*N*'-dibutyl-*N*,*N*'-bis(4-methylphenylsulfonyl hydrazide) 11 have a high antibacterial and antifungal activity. Compounds 4, 5, and 11 are oil-soluble; hence, they can be used for protection of petroleum products against biodegradation. Quaternary ammonium salts of monosulfonyl hydrazides 6 and 7 also exhibit a high bactericidal and fungicidal activity; this fact proves that ammonium salts are promising for protection of lubricating fluids from biological degradation.

In summary, it has been found that the investigational arylsulfonyl hydrazides exhibit good antimicrobial properties and their performance is higher than that of the known biocides used in industry.

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