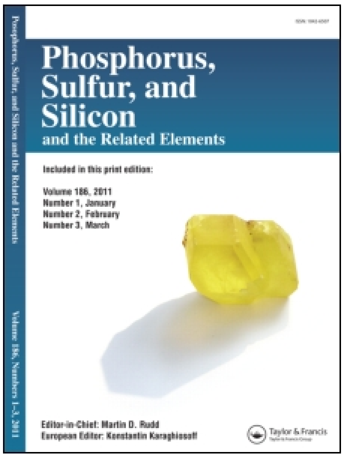

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SYNTHESES WITH SULFUR CONTAINING NUCLEOPHILES. I. REACTION OF SULFINIC ACIDS WITH 2-HALOGENO-2-NITROETHENYLARENES

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SYNTHESES WITH SULFUR CONTAINING NUCLEOPHILES. I. REACTION OF SULFINIC ACIDS WITH 2-HALOGENO-2-NITROETHENYLARENES

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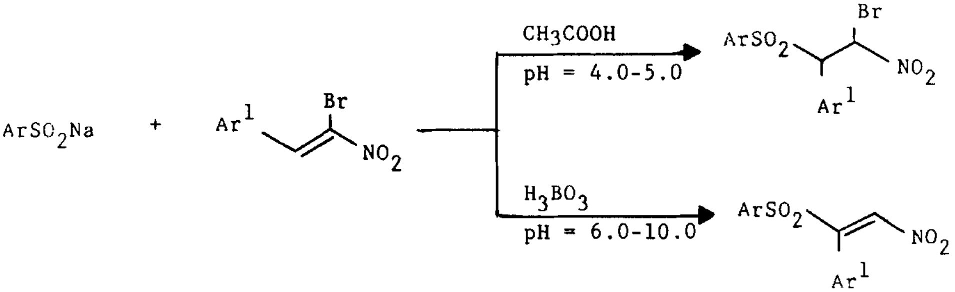
The interaction between unsubstituted and *p*-substituted benzenesulfinic acids and various 2-halogeno-2-nitroethenylarenes at mol ratios sulfinic acid:2-halogeno-2-nitroethenylarene = 1:1 and 2:1 was studied at 0°C and 20°C for 16 and 96 hours. It was proved that, depending on experimental conditions, the reaction results not only in α-halogeno-α-nitro-β-sulfones but also in α-nitro-α,β-disulfones, which are obtained by a consecutive process. The quantitative ratio of these products and the isomer composition of some of them were determined by using high-performance liquid chromatography (HPLC).

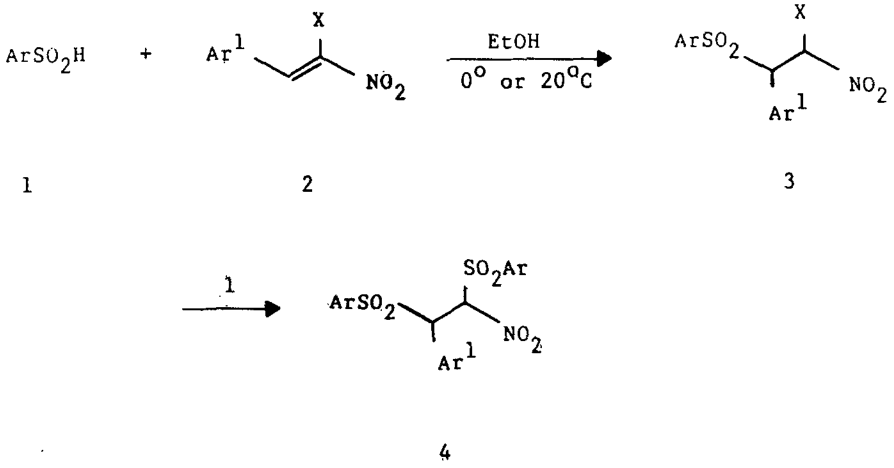
Key words: Sulfinic acids, 2-halogeno-2-nitroethenylarenes, HPLC, α-halogeno-α-nitro-β-nitro-β-sulfones, α-nitro-α,β-disulfones, α-diastereomers.

INTRODUCTION

A number of publications[1] dealing with the addition of various nucleophilic reagents to 2-halogeno-2-nitroethenylarenes are available. The interaction of the latter with sulfinic acids was studied in a few works.[2–3] It was reported by one of us[3] that when suitable buffer systems are used, sulfinic acids react with 2-bromo-2-nitroethenylarenes and addition compounds or dehydrobromation products of the latter are obtained.



Our aim was now to study the same reaction in the absence of buffer systems at various mol ratios of initial reagents, various temperatures and longer duration. Changing the reaction condition we expected not only to synthesize new α-halogeno-α-nitro-β-sulfones **3** but also to outline suitable conditions for substituting the halogen atom in α-halogeno-α-nitro-β-sulfones **4** by another sulfonyl group without the necessity of isolating the addition compounds from the reaction mixture.



1	Ar	2	Ar^1	X	2	Ar^1	X
a	Ph	a	Ph	Cl	e	4-MeOC_6H_4	Br
b	4-MeC_6H_4	b	Ph	Br	f	$3\text{-O}_2NC_6H_4$	Cl
c	4-ClC_6H_4	c	4-MeC_6H_4	Cl	g	$3\text{-O}_2NC_6H_4$	Br
		d	4-MeC_6H_4	Br	h	$4\text{-O}_2NC_6H_4$	Cl
					i	$4\text{-O}_2NC_6H_4$	Br

3	Ar	Ar^1	X	3	Ar	Ar^1	X
a	Ph	Ph	Cl	n	4-MeC_6H_4	4-MeOC_6H_4	Br
b	4-MeC_6H_4	Ph	Cl	o	4-ClC_6H_4	4-MeOC_6H_4	Br
c	4-ClC_6H_4	Ph	Cl	p	Ph	$3\text{-O}_2NC_6H_4$	Cl
d	Ph	Ph	Br	q	4-MeC_6H_4	$3\text{-O}_2NC_6H_4$	Cl
e	4-MeC_6H_4	Ph	Br	r	4-ClC_6H_4	$3\text{-O}_2NC_6H_4$	Cl
f	4-ClC_6H_4	Ph	Br	s	Ph	$3\text{-O}_2NC_6H_4$	Br
g	Ph	4-MeC_6H_4	Cl	t	4-MeC_6H_4	$3\text{-O}_2NC_6H_4$	Br
h	4-MeC_6H_4	4-MeC_6H_4	Cl	u	4-ClC_6H_4	$3\text{-O}_2NC_6H_4$	Br
i	4-ClC_6H_4	4-MeC_6H_4	Cl	v	Ph	$4\text{-O}_2NC_6H_4$	Cl
j	Ph	4-MeC_6H_4	Br	w	4-MeC_6H_4	$4\text{-O}_2NC_6H_4$	Cl
k	4-MeC_6H_4	4-MeC_6H_4	Br	x	4-ClC_6H_4	$4\text{-O}_2NC_6H_4$	Cl
l	4-ClC_6H_4	4-MeC_6H_4	Br	y	Ph	$4\text{-O}_2NC_6H_4$	Br
m	Ph	4-MeOC_6H_4	Br	z	4-MeC_6H_4	$4\text{-O}_2NC_6H_4$	Br

4	Ar	Ar^1	4	Ar	Ar^1
a	Ph	Ph	i	4-ClC$_6$H$_4$	3-O$_2$NC$_6$H$_4$
b	4-MeC$_6$H$_4$	Ph	j	Ph	4-O$_2$NC$_6$H$_4$
c	4-ClC$_6$H$_4$	Ph	k	4-MeC$_6$H$_4$	4-O$_2$NC$_6$H$_4$
d	Ph	4-MeC$_6$H$_4$	l	4-ClC$_6$H$_4$	4-O$_2$NC$_6$H$_4$
e	4-MeC$_6$H$_4$	4-MeC$_6$H$_4$	m	Ph	4-MeOC$_6$H$_4$
f	4-ClC$_6$H$_4$	4-MeC$_6$H$_4$	n	4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$
g	Ph	3-O$_2$NC$_6$H$_4$	o	4-ClC$_6$H$_4$	4-MeOC$_6$H$_4$
h	4-MeC$_6$H$_4$	3-O$_2$NC$_6$H$_4$			

In the course of the experiments, neither products of dehydrobromation nor ethoxy-derivatives of **3** were obtained. Synthesis of nitroalkenylsufones is possible under more special conditions.[4] Moreover, parallel experiments showed that products **3** obtained in aqueous-dioxane medium (1:2, 5) do not change into the corresponding ethoxy-derivatives no matter how long they stay in ethanol (7 days).

The new tetrasubstituted ethanes have two different asymmetric centres. It was also interesting to study the change in the quantitative ratio between final products **3** and **4** depending on experimental conditions and the structure of the starting 2-halogeno-2-nitroethenylarenes **2**. In order to achieve this goal, it was necessary to vary the mol ratios between 1 and 2 and to prolong the reaction time in some cases.

RESULTS AND DISCUSSION

The results from the study of the interaction between unsubstituted and *p*-substituted benzenesulfinic acids **1a–c** (donor) and various 2-halogeno-2-nitroethenylarenes **2a–i** (acceptor) at mol ratios sulfinic acid:2-halogeno-2-nitroethenylarene = 1:1 and 2:1 are presented in this work. The 2-halogeno-2-nitroethenylarenes 2 chosen contain different halogen atoms (**2**, X = Cl, Br) at the double bond. The phenyl moiety both in **1** and **2** is unsubstituted or substituted by typical electron-donating or electron-withdrawing substituents. The reaction was studied in ethanol solution at 0°C and 20°C for 16 or in some cases for 96 hours.

The experimental results show that the reaction between sulfinic acids **1a–c** and 2-halogeno-2-nitroethenylarenes **2a–i** yield either addition compounds **3a–z** which can undergo further substitution reaction leading to *α*,*β*-disulfones **4a–o** depending on the experimental conditions and the nature of acceptor **2a–i**. The quantitative ratio between products **3** and **4** was determined by using high-performance liquid chromatography (Table I). The HPLC control of the reaction between sulfinic acids **1a–c** and 2-halogeno-2-nitroethenylarenes **2a–e** with phenyl either unsubstituted or substituted with an electron-donating substituent shows that the only products obtained at equimolar ratio of the initial reagents, 20°C and duration of the reaction from 16 to 96 hours, are the addition products **3a–o**. Under the same conditions but with a 100% excess of sulfinic acids, the ratio between addition products **3a–l** and **4a–l** (addition followed by substitution) changes in favour of the latter. The

TABLE I

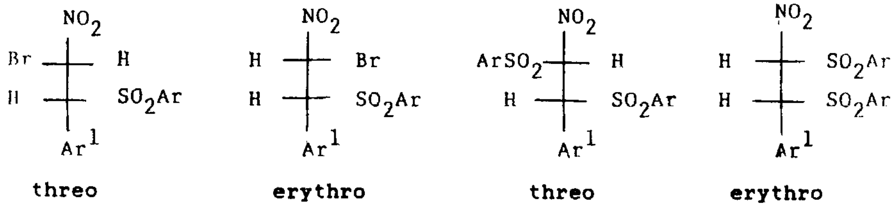
Data obtained by studying the reaction between sulfinic acids **1a–c** and 2-halogeno-2-nitroethenylarenes **2a–i** by means of high-performance liquid chromatography

Starting substances		Yield (%) of reaction products 3 and 4 at different mol ratios sulfinic acids : 2-halogeno-2-nitroethenylarene				Experimental conditions	
						Duration h	Temperature °C
1	2	1 : 1		2 : 1			
		3	4	3	4		
a	a	a 92	a 0	a 9	a 81	16	20
b	a	b 85	b 0	b 8	b 89	16	20
c	a	c 77	c 0	c 16	c 68	16	20
a	b	d 85	a 0	d 6	a 87	16	20
b	b	e 88	b 0	e 2	b 94	16	20
c	b	f 79	c 0	f 12	c 72	16	20
a	c	g 69	d 0	g 18	d 64	16	20
b	c	h 72	e 0	h 8	e 68	16	20
c	c	i 70	f 0	i 17	f 60	16	20
a	d	j 78	d 0	j 10	d 76	16	20
b	d	k 81	e 0	k 7	e 79	16	20
c	d	l 84	f 0	l 13	f 65	16	20
a	e	m 61	m 0	m 66	m 0	96	20
b	e	n 64	n 0	n 69	n 0	96	20
c	e	o 56	o 0	o 60	o 0	96	20
a	f	p 76	g 12	p 0	g 82	16	0
b	f	q 65	h 34	q 0	h 92	16	0
c	f	r 71	i 20	r 0	i 89	16	0
a	g	s 0	g 71	s 0	g 89	16	0
b	g	t 0	h 84	t 0	h 91	16	0
c	g	u 0	i 79	u 0	i 86	16	0
a	h	v 0	j 71	v 0	j 85	16	0
b	h	w 0	k 79	w 0	k 89	16	0
c	h	x 0	l 83	x 0	l 87	16	0
a	i	y 0	j 67	y 0	j 87	16	0
b	i	z 0	k 73	z 0	k 91	16	0

c	h	x 0	l 83	x 0	l 87	16	0
a	i	y 0	j 67	y 0	j 87	16	0
b	i	z 0	k 73	z 0	k 91	16	0

only exception is the sole addition of **1a–c** at the more electron rich acceptor **2e** (Ar^1 = 4-$MeOC_6H_4$) leading to the compounds **3m–o**.

The tendency of forming disulfones **4** increases considerably when the acceptor **2** becomes more electron deficient (Ar^1 = $NO_2C_6H_4$). This is illustrated by the exclusive formation of disulfones **4g–l** in the reaction between **1a–c** and **2g–i** at 0°C irrespective to the mol ratios (1:1 or 2:1). Under these conditions, addition compounds **3p–r** were isolated only is case of 1-nitro-3-(2-chloro-2-nitroethenyl)benzene **2f** as acceptor. With 2 equivalent of **1a–c** disulfones **4p–r** were obtained again. These results show the clear dependence between the ratio of the reaction products **3** and **4** and the structure of the initial acceptor **2**.



3 d,j,p **4 a,d,j**

Tetrasubstituted ethanes resulting from these reactions have two asymmetric carbon atoms. Our attempts to separate these isomers by column chromatography on silica gel failed. The study of some of these compounds (Table II) by means of liquid chromatography showed that they are mixtures of threo- and erythro-isomers.

α-Halogeno-α-nitro-β-sulfones **3a–z** and α-nitro-α,β-disulfones **4a–o** are colourless crystalline substances, highly soluble in acetone and dioxane, and moderately in ethanol (Tables III and IV).

TABLE II

Isomer composition of some of the products **3** and **4**

Product	Isomer composition (%)		Product	Isomer composition (%)	
	threo	erythro		threo	erythro
3d	53	47	4a	69	31
3j	52	48	4d	63	37
3p	57	43	4j	66	34

TABLE III

Physical and spectroscopic data of compounds 3a–r

Product	mp (°C) (EtOH)	Molecular Formula	IR (KBr) ν (cm -1)
a	114	$C_{14}H_{12}ClNO_4S$	1560,1345,1320,1130,1090
b	132	$C_{15}H_{14}ClNO_4S$	1555,1350,1320,1140,1090
c	130	$C_{14}H_{11}ClNO_4S$	1550,1340,1325,1130,1080

TABLE III (*Continued*)

Product	mp (°C) (EtOH)	Molecular Formula[a]	IR (KBr) ν (cm⁻¹)
g	143	$C_{15}H_{14}ClNO_4S$	1550,1360,1330,1120,1090
h	139	$C_{16}H_{16}ClNO_4S$	1545,1355,1320,1140,1080
i	149-150	$C_{15}H_{13}Cl_2NO_4S$	1550,1350,1320,1135,1080
j	138-139	$C_{15}H_{14}BrNO_4S$	1555,1345,1315,1150,1080
k	129	$C_{16}H_{16}BrNO_4S$	1550,1360,1320,1140,1080
m	145	$C_{15}H_{14}BrNO_5S$	1540,1355,1345,1150,1090
n	137	$C_{16}H_{16}BrNO_5S$	1550,1360,1340,1160,1080
o	151	$C_{15}H_{13}ClBrNO_5S$	1545,1350,1340,1150,1080
p	140	$C_{14}H_{11}ClN_2O_6S$	1510,1350,1305,1150,1080
q	135	$C_{15}H_{13}ClN_2O_6S$	1510,1355,1300,1150,1085
r	153	$C_{14}H_{10}Cl_2N_2O_6S$	1505,1350,1300,1140,1085

[a] Satisfactory microanalyses obtained: C+ 0.30, H+ 0.25, N+ 0.20, S± 0.30.

TABLE IV

Physical and spectroscopic data of compounds **4a–l**

Product	mp (°C) ethanol/dioxane,10:1	Molecular Formula[a]	IR (KBr) ν (cm⁻¹)
a	186-187	$C_{20}H_{17}NO_6S_2$	1550,1340,1320,1140,1080
b	127	$C_{22}H_{21}NO_6S_2$	1560,1350,1320,1130,1080
c	156	$C_{20}H_{15}Cl_2NO_6S_2$	1555,1345,1320,1135,1090
d	179	$C_{21}H_{19}NO_6S_2$	1560,1340,1325,1130,1080
e	163	$C_{23}H_{23}NO_6S_2$	1550,1350,1330,1140,1090
f	167	$C_{20}H_{17}Cl_2NO_6S$	1550,1340,1320,1130,1090
g	146	$C_{20}H_{16}N_2O_8S_2$	1510,1355,1330,1135,1080
h	151-152	$C_{22}H_{20}N_2O_8S_2$	1510,1350,1320,1140,1080
i	162	$C_{20}H_{15}Cl_2N_2O_8S_2$	1510,1355,1340,1150,1080
j	160	$C_{20}H_{16}N_2O_8S_2$	1505,1350,1330,1140,1090
k	152	$C_{22}H_{20}N_2O_8S_2$	1510,1340,1320,1145,1090
l	164-165	$C_{20}H_{14}Cl_2N_2O_8S_2$	1510,1355,1335,1140,1080

[a] Satisfactory microanalyses obtained: C± 0.30, H± 0.25, N± 0.20, S± 0.30.

EXPERIMENTAL

The starting substances **1a–c**[5] and **2a–i**[6–9] were prepared by known procedures. Melting points were measured on a microstage block and are uncorrected. Microanalyses were determined using an Elemental Analyser-1104 (Carlo Erba, Italy). IR spectra were obtained on a Specord 75 IR apparatus (Germany). HPLC was performed using a Series-4 apparatus (Perkin-Elmer) and a programmable multiwavelength detector. Liquid-chromatographic analysis of the total crude product and the filtrate in each case was performed by using RP-8 column, eluent CH_3OH/H_2O (60/40), at flow rate 1 ml/min. HPLC separation of threo- and erythro-isomers was carried out at 254 nm using a UV detector. Column chromatography was performed using gel L 100/250 (Lachema, Chematol, Czechoslovakia).

Typical Procedures

α-Halogeno-α-Nitro-β-Sulfones **3a–z**. 0.001 g-mol sulfinic acid **1a–c** was added to a soluton of 0.001 g-mol 2-halogeno-2-nitro-ethenylarene **2a–i** in 5 ml ethanol. This solution (pH = 3) was kept at 20°C for 16 hours. The reaction between 1-nitro-3-(2-chloro-2-nitroethenyl)benzene **2f** and sulfinic acids took place at 0°C for 16 horus, and 1-methoxy-4-(2-bromo-2-nitroethenyl)benzene **2e** reacted with the same acids for 96 hours at 20°C. The crystals obtained were filtered and recrystallized from ethanol.

α-Nitro-α,β-Disulfones **4a–o**. 0.001 g-mol sulfinic acid **1a–c** was added to a solution of 0.001 g-mol 2-halogeno-2-nitroethenylarene **2a–i** in 5 ml ethanol. The reaction mixture was kept at 20°C for 16 hours and then the crystals obtained were filtered and recrystallized from ethanol. 1-Nitro-3-(2-bromo-2-nitroethenyl)benzene **2g**, 1-nitro-4-(2-bromo-2-nitroethenyl)benzene **2i** reacted with sulfinic acids at 0°C for 16 hours. The crystals obtained were filtered and recrystallized from ethanol:dixoane = 10:1.

REFERENCES

1. V. V. Perekalin, A. S. Sopova and E. S. Lipina, "Nepredel'nie soedinenia," Khimia, Leningradskoe otdelenie, 1982, p. 204.
2. D. I. Aleksiev, *Zh. Org. Khim.*, **11**, 211 (1975); Ibid., **11**, 908 (1975).
3. D. I. Aleksiev, "XXX Gercenovskie tchtenia," Leningrad, 1976, p. 63.
4. D. I. Aleksiev and S. Ivanova, Eighth European Symposium on Organic Chemistry, Sitges, Barcelona, 1993, p. 465.
5. Y. Ogata, Y. Sawaki and M. Isono, *Tetrahedron*, **25**, 2715 (1969).
6. B. Prieds, *Lieb. Ann.*, **225**, 319, 329 (1884).
7. P. Pfeiffer, *Chem. Ber.*, **47**, 1755 (1914).
8. D. Warrall, *J. Amer. Chem. Soc.*, **66**, 842 (1944).
9. J. Thele, *Liebs. Ann.*, **377**, 1 (1910).