

SPECTRAL STUDIES OF SOME HALOGENATED NITROSULFONE DERIVATIVES (PART I)

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ABSTRACT

A series of halogen-containing derivatives of p-substituted arylnitrosulfones was prepared as a result from the nucleophilic addition of sulfinic acids to β -bromo- β -nitrostyrene. The effects of various substituents in the molecules of both the sulfinic acids and nitroalkene reactants on the spectral characteristics of the sulfone products were studied.

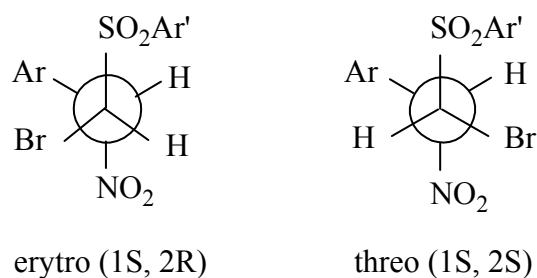
Keywords: β -bromo- β -nitrostyrene, sulfones, structure, nucleophilic addition.

INTRODUCTION

Sulfinic acids are known to possess unique properties as nucleophiles that cause facile nucleophilic addition interactions with compounds, possessing active carbon-carbon double bonds [1]. Many of our previous studies have been devoted to these Michael-type addition reactions and as a result, various types of organosulfur compounds such as aliphatic nitrosulfones, arylnitrosulfones, and the corresponding halogenated derivatives, etc. have been synthesized. The present work extends the scope of the arylnitrosulfones obtained and aims at further and more detailed studies on their possible characteristics and application.

DISCUSSION

1-Aryl-2-arylsulfonyl-2-bromo-1-nitroethane derivatives are interesting compounds in terms of studying the influence of two or three electron-withdrawing substituents on their vibrational spectra. The stereochemistry of such organic chemicals is also regarded as worth studying, due to the presence of two chiral centers in their molecular structures.



Ar = 4-MeC₆H₄; Ar' = Ph, 2-MeC₆H₄; 4-MeOC₆H₄;
 4-ClC₆H₄; 4-BrC₆H₄; 4-IC₆H₄; 4-NO₂C₆H₄,
 1-,2-C₁₀H₇, 4-AcNHC₆H₄

IR-spectra of the compounds studied indicated strong absorption bands, which are characteristics for both the nitro- and sulfonyl functional groups. Moreover, a trend towards an increase of the frequencies of the symmetric ones for the nitro group was observed. No significant changes in this respect were found for the sulfonyl group. The high intensities of these characteristic bands should be expected, bearing in mind the geometry of the sulfonyl group with its out-of-plane location with respect to the other substituents. The IR spectra of these particular organosulfur compounds confirmed the common knowledge that the sulfonyl group cannot be considered as analogous to the carbonyl one, due to the differences in their symmetry and electron structure. The spectral studies did not reveal any existence of conjugation between the sulfonyl- and nitro groups, which should be expected from their location at different planes. The stretching vibrations of the carbon-halogenated bond were observed within the 640-680 cm⁻¹ region. The presence of halogen at alpha-position with respect to the nitro group did not effect the position of the characteristic vibrations of the nitro- and sulfonyl groups. Medium- intensity absorption band at 1090 - 1080 cm⁻¹ was also observed, which could be assigned to the stretching S-aryl vibrations. Triplet with decreasing intensity of the bands with higher frequencies appeared at 3120 - 3000 cm⁻¹, which are characteristic for the C - H, stretching vibrations of mono- substituted benzene ring. For p-substituted ones, the bands at 825 - 805 cm⁻¹ were also indicative.

The presence of methyl groups at p-position was characterized by the asymmetric and symmetric stretching vibrations at 2950 and 2830 cm⁻¹, respectively. The methoxy group at p-position in the benzene ring was, on the other hand, proved by the characteristic stretching vibrations of the CH₃-group in methyl phenyl esters at 2845 cm⁻¹ and, also, by the bands at 1275 and 1025 cm⁻¹, corresponding to - C - O - C - fragment. The band at 855 - 845 cm⁻¹ could be assigned to stretching C - N vibration. Deformation C - H vibration, corresponding to three neighboring hydrogen atoms in the alpha-naphtylsulfonyl group were observed at 810 - 785 cm⁻¹. The introduction of halogen atom into the phenylsulfonyl group resulted in the appearance of characteristic for secondary were observed at 1720 - 1520 cm⁻¹.

Table 1. Characterization data of the compounds

Comp №	m.p. °C	Formula mol.wt	Analysis (%) calc (found)				IR(ν , cm^{-1}) KBr	$^1\text{H NMR}$ (CDCl_3 ,
			C	H	N	S		
1	144-145	$\text{C}_{15}\text{H}_{14}\text{BrNO}_4\text{S}$ (384)	46.88 (45.90)	3.65 (3.20)	3.65 (3.13)	8.33 (8.10)	1560-1340 (NO_2) 1320-1140 (SO_2)	7.20-7.80 (m, 9H) 5.10 (d,CH), 6.20 (d, CH), 2.40 (s, CH_3)
2	147-149	$\text{C}_{16}\text{H}_{17}\text{BrNO}_4\text{S}$ (399)	48.12 (47.50)	4.26 (4.12)	3.51 (3.10)	8.02 (7.75)	1550-1330 (NO_2) 1315-1135 (SO_2)	7.25-7.82 (m, 8H) 5.16 (d,CH), 6.20 (d, CH), 2.42 (s, CH_3)
3	152-153	$\text{C}_{16}\text{H}_{16}\text{BrNO}_5\text{S}$ (404)	47.52 (47.10)	3.96 (3.65)	3.46 (3.20)	7.92 (7.35)	1555-1340 (NO_2) 1310-1135 (SO_2)	7.22-7.80 (m, 8H) 5.15 (d,CH), 6.22 (d, CH), 2.42 (s, CH_3)
4	149-150	$\text{C}_{15}\text{H}_{13}\text{ClBrNO}_4\text{S}$ (418.5)	43.01 (42.60)	3.11 (2.70)	3.35 (2.80)	7.65 (7.15)	1550-1345 (NO_2) 1315-1130 (SO_2)	7.26-7.84 (m, 8H) 5.16 (d,CH), 6.20 (d, CH), 2.42 (s, CH_3)
5	161-162	$\text{C}_{15}\text{H}_{13}\text{Br}_2\text{NO}_4\text{S}$ (463)	38.88 (38.25)	2.81 (2.30)	3.02 (2.60)	6.91 (6.35)	1550-1340 (NO_2) 1310-1140 (SO_2)	7.28-7.88 (m, 8H) 5.15 (d,CH), 6.22 (d, CH), 2.40 (s, CH_3)
6	187-188	$\text{C}_{15}\text{H}_{13}\text{BrINO}_4\text{S}$ (510)	35.29 (34.70)	2.55 (2.10)	2.75 (2.30)	6.27 (5.85)	1550-1335 (NO_2) 1320-1140 (SO_2)	7.26-7.80 (m, 8H) 5.20 (d,CH), 6.20 (d, CH), 2.40 (s, CH_3)
7	192	$\text{C}_{15}\text{H}_{13}\text{BrN}_2\text{O}_6\text{S}$ (429)	41.96 (40.60)	3.03 (2.50)	6.53 (6.10)	7.46 (7.20)	1550-1340 (NO_2) 1310-1130 (SO_2)	7.22-7.84 (m, 8H) 5.18 (d,CH), 6.21 (d, CH), 2.40 (s, CH_3)
8	196-197	$\text{C}_{19}\text{H}_{16}\text{BrNO}_4\text{S}$ (434)	52.53 (51.70)	3.69 (3.15)	3.22 (2.80)	7.37 (7.12)	1555-1330 (NO_2) 1320-1140 (SO_2)	7.25-7.80 (m, 8H) 5.20 (d,CH), 6.20 (d, CH), 2.40 (s, CH_3)
9	204-205	$\text{C}_{17}\text{H}_{17}\text{BrN}_2\text{O}_5\text{S}$ (441)	46.26 (45.80)	3.85 (3.40)	6.35 (6.10)	7.26 (7.50)	1560-1340 (NO_2) 1320-1135 (SO_2)	7.22-7.80 (m, 8H) 5.20 (d,CH), 6.20 (d, CH), 2.40 (s, CH_3)

NMR spectra of the compounds obtained were characterized mainly by the aromatic multiplets within 7.20 – 7.85 ppm. Moreover, two doublets corresponding to methyne protons within 5.00 – 5.20, and 3.00 – 3.35, and 2.80 – 3.15 ppm, depending on the type of halogen, were observed. The corresponding integral curves indicated that each doublet corresponded to one proton.

EXPERIMENTAL

Halogenated nitrosulfone derivatives were prepared and purified as described in the literature [2].

IR and UV spectra were obtained using Bruker and Specord UV-VIS. NMR (chemical shifts measured in deuterated solvents are given in ppm from TMS) spectra were recorded with a Bruker 350 MHz spectrometer, using CDCl₃ solution.

REFERENCES

1. The Chemistry of Sulfinic acids, esters and their derivatives, Ed. By S.Patai, 1990, John Wiley & Sons Ltd.
2. Perekalin V.V., E. S. Lipina, V.M. Berestovitskaya, D.A. Efremov, Nitroalkenes. Conjugated Nitrocompounds, London. John Wiley & Sons, 1994.