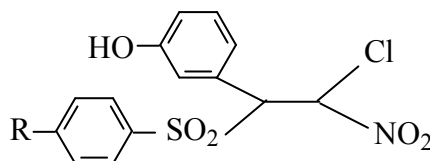


NUCLEOPHILIC REACTION OF SULFINIC ACIDS WITH 4-HYDROXY-β-CHLORO-β-NITROSTYRENETHE

Assoc.Prof. Sonya Ivanova

Department of Organic Chemistry,
University Prof. Assen Zlatarov, Bulgaria
Tel.: +00356 886 322 335
E-mail: viperorg@abv.bg

Abstract: The nucleophilic addition of arenesulfinic acids with 4-hydroxy-β-chloro-β-nitrostyrene have been studied. The general formula of the compounds obtained was follows:



The composition and structure of the sulfones were confirmed by elemental microanalysis and different spectral methods.

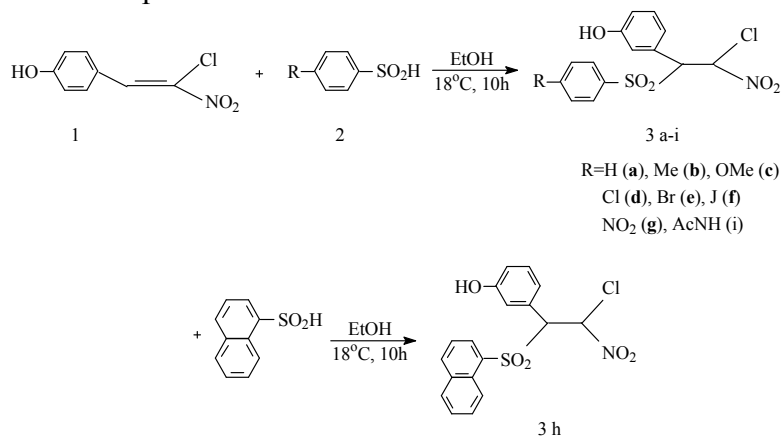
Keywords: Nucleophilic addition, Sulfinic acids, Nitrosulfones.

INTRODUCTION

Sulfinic acids as serve as unique example for reactants, undergoing facile nucleophilic addition to σ , β -unsaturated compounds, which results in the formation of Michael-type products. (Schank, K. Patai, S., & Rappoport, Z., 1988). This method of production sulfones has a number of advantages. The presence of different functional groups in the sulfones determined broad synthetic possibilities for the preparation of substances with desirable chemical and biological properties. (Drabowicz, J. Kiebasinski, P., & Mikolajczyk, M., Kotler, P., 1990). The present work extends this reaction to the synthesis of polyfunctional sulfones.

EXPOSITION

The interaction of arenesulfinic acids with 4-hydroxy-β-chloro-β-nitrostyrene occurs according to the reactions depicted in Scheme 1.



The addition starts with nucleophilic attack to ward the β -carbon atom of the double carbon-carbon bond. The second step is the protonaton of the carbanion formed and, consequently, the end product formation. The suggested method of obtaining arylsulfonylnitroethanes has some important

advantages over the methods know so far: it is a relatively short, one stage process, no by-products are obtained, so there is no need of further procedures to separate the main products from the reaction mixture the final compounds possess a good degree of purity.

Sulfones 3a-h are synthesized as results of the interaction of equimolar amounts of the corresponding reagents in ethanol at room temperature for 10h. The crystalline products obtained were filtered and purified by recrystallization from dioxane. The products were found to be stable on prolonged storage in air and were soluble in acetone, chloroform but insoluble in water, n-hexane and petroleum ether. The yields obtained varied the range 93-96%.

Table 1. Physical and analytical data for compounds

№	Yield (%)	Tm (°C)	Molecular Formula	Molar mass (g.mol ⁻¹)	Analysis calc. (found) (%)			
					C	H	N	S
3a	97	169	C ₁₄ H ₁₄ ClNO ₅ S	344	48.91 48.60	4.08 3.80	4.07 3.75	9.32 9.12
3b	94	172	C ₁₅ H ₁₄ ClNO ₅ S	356	50.63 49.94	3.94 3.75	3.94 3.82	9.00 9.89
3c	98	174	C ₁₅ H ₁₄ ClNO ₆ S	372	48.45 48.29	3.77 3.70	3.77 3.64	8.61 8.56
3d	96	177.5	C ₁₄ H ₁₁ Cl ₂ NO ₅ S	376	44.68 44.35	2.92 2.70	3.72 2.68	8.51 8.36
3e	97	183.5	C ₁₄ H ₁₁ ClBrNO ₅ S	421	39.95 39.77	2.62 2.50	3.33 3.12	7.61 7.37
3f	93	186.5	C ₁₄ H ₁₁ ClINO ₅ S	468	35.94 35.79	2.35 2.18	2.99 2.78	6.84 6.80
3g	94	159	C ₁₄ H ₁₁ ClN ₂ O ₇ S	387	43.47 43.25	2.85 2.69	3.62 3.56	8.28 8.09
3h	96	191	C ₁₈ H ₁₄ ClNO ₅ S	392	55.17 54.96	3.57 3.39	3.57 3.41	8.17 8.02
3i	93	164	C ₁₆ H ₁₅ ClN ₂ O ₆ S	399	48.18 48.06	3.76 3.59	3.51 3.39	8.03 7.89

IR-spectra of the compounds studied display strong absorption bands, characteristic for both the NO₂ and SO₂ functional groups. The high intensities of these characteristic bands should be expected, having in mind the geometry of the SO₂ group with its out-of-plane location with respect to the other substituent. The spectral studies did not reveal any existence of conjugation between the SO₂ and NO₂ groups, which should be expected from their location at different planes. Medium-intensity absorption bands at 1090-1080 cm⁻¹ was also observed, which could be assigned to the stretching S-aryl vibration. The band at 855-845 cm⁻¹ could be assigned to stretching C-N vibration. Deformation C-H vibrations, corresponding to three neighboring hydrogen atoms in SO₂C₁₀H₇ group, observed at 805-790 cm⁻¹. Skeletal vibrations of the benzene ring were characterized by the bands at 1645-1455 cm⁻¹, and out-of-plane C-H aryl vibration within 720 cm⁻¹ and 790 cm⁻¹ proved the presence of monosubstituted and disubstituted benzene ring, respectively.

In $^1\text{H-NMR}$ spectra, multiples characteristic for the aromatic protons are observed in region of 7.20-7.80 ppm. In the case of 3 the protons of the ethane unit appear as doublet at 5.15-5.17 ppm, 6.20-6.22 ppm, respectively.

Table2. Spectroscopic data for compounds

No	IR data ν (cm^{-1})	$^1\text{H-NMR}$ (CDCl_3) δ (ppm)
3a	1560,1355 (NO_2), 1320-1130 (SO_2), 3600 (O-H), 1225 (C-O)	7.20-7.70 (m, 9H); 5.13 (d, CH); 6.20 (d, CH), 4.5 (O-H)
3b	1565,1355 (NO_2), 325,1135(SO_2), 3610 (O-H), 1220 (C-O)	7.21-7.72 (m, 8H); 5.12 (d, CH); 6.18 (d, CH); 4.51 (O-H)
3c	1565,1355 (NO_2); 1320,1140 (SO_2); 3612 (O-H); 1220 (C-O)	7.23-7.70 (m, 8H); 5.12 (d, CH); 6.15 (d, CH); 4.55 (O-H)
3d	1565,1350 (NO_2); 1320,1140 (SO_2); 3610 (O-H); 1225 (C-O)	7.21-7.73 (m, 8H); 5.11 (d, CH); 6.17 (d, CH); 4.52 (O-H)
3e	1565,1355 (NO_2); 1320,1135 (SO_2); 3615 (O-H); 1225 (C-O)	7.25-7.70 (m, 8H); 5.15 (d, CH); 6.15 (d, CH); 4.50 (O-H)
3f	1560,1355 (NO_2); 1320-1130 (SO_2); 3612 (O-H); 1227 (C-O)	7.25-7.72 (m, 8H); 5.15 (d, CH); 6.12 (d, CH); 4.55 (O-H)
3g	1565,1350 (NO_2); 1320,1140 (SO_2); 3610 (O-H); 1225 (C-O)	7.20-7.75 (m, 8H); 5.16 (d, CH); 6.15 (d, CH); 4.55 (O-H)
3h	1565,1355 (NO_2); 1325-1135 (SO_2); 3615 (O-H); 1225 (C-O)	7.25-7.70 (m, 11H); 5.15 (d, CH); 6.15 (d, CH); 4.52 (O-H)

CONCLUSION

1. A series of nitrosulfones was synthesized by nucleophilic addition of sulfinic acids to 4-hydroxy- β -chloro- β -nitrostyrene.
2. The composition and structure of the sulfones were confirmed by elemental microanalysis and different spectral methods.
3. The nucleophilic activity of sulfinic acids increases with the introduction of electron-donating substituents and decreases in the presence of electron-withdrawing substituents.

REFERENCES

- Schank, K., Patai, S., & Rapport, Z. (1988). *The Chemistry of Sulfones and Sulfoxides*. New York.
- Drabowicz, J., Kielbasinski, P., & Mikolajczyk, M., in Patai, S. (Ed.). (1990). *The Chemistry of Sulfinic Acids, Esters and Derivatives*, 12, 370-374.