

NUCLEOPHILIC ADDITION OF SULFINIC ACIDS TO 4-FLUORO- β -CHLORO- β -NITROSTYRENE

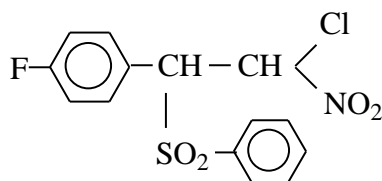
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ABSTRACT

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.

Key words: nucleophilic addition, sulfones, heteroconjugated alkenes

INTRODUCTION

Sulfinic acids add easily to conjugated Michael-type alkenes to yield the corresponding β -substituted sulfones [1].

The aim of the present study was to examine the structural characteristics of series of sulfones prepared by known methods middle conditions.

MATERIALS AND METHODS

Melting points are uncorrected. IR spectra (KBr) were recorded with a Bruker spectrophotometer. $^1\text{H-NMR}$ spectra were recorded with Bruker (350 MHz) spectrometer using CDCl_3 as solvent and TMS as internal standard. Microanalytically data were obtained using an elemental Analyzer – 1104 (Carlo-Erba).

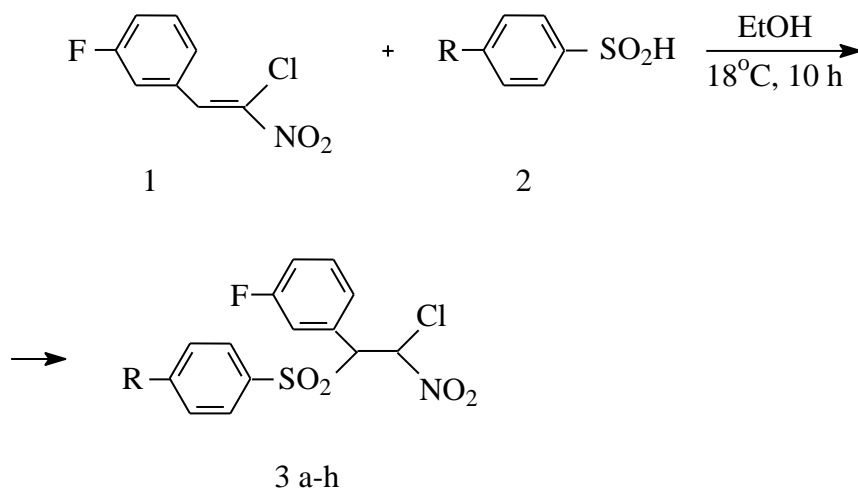
Sulfinic acids and 4-fluoro- β -chloro- β -nirtostyrene were prepared and purified as described in the literature [2].

Synthesis of Compounds: General Procedure. To the nitro alkene (0.1 moll) in 95% ethanol was added the corresponding sulfinic acids (0.1 moll). The reaction mixture was kept

standing at 18⁰C for 10 h. The crystalline products obtained were filtered and purified by recrystallization from dioxane\benzene.

RESULTS AND DISCUSSION

The interaction of arenesulfonic acids with 4-fluoro-β-chloro-β-nitrostyrene occurs according to the reactions in scheme.



Compounds 3a-h are obtained by mixing equimolar amounts of 1 and 2 in medium of ethanol. The yields are 95-97% and there are no by-products. These compounds are colorless, crystalline substances and very soluble in chloroform, acetone and dioxane. They are stable in long storage and melt without decomposition. The compounds were unaltered by TLC. Their composition was determined by microanalytical methods (all compounds give satisfactory elemental analysis, Table 1).

IR spectra of the compounds studied indicated strong absorption bands, which are characteristic 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 geometry of the sulfonyl group with out-of-plane location with respect to the other substituents. The IR spectra of these particular organosulfur compounds confirm the common knowledge that the sulfonyl group cannot be considered 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. Medium intensity absorption band 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 vibration, corresponding to three neighboring hydrogen atoms in the

naphtylsulfonyl group were observed at $810\text{-}785\text{ cm}^{-1}$. Skeleton vibrations of benzene ring were characterized by the bands at $1640\text{-}1450\text{ cm}^{-1}$, and out-of-plane C-H aryl vibration within $725\text{-}720\text{ cm}^{-1}$ and 810 cm^{-1} proved the presence of mono-substituted and p-substituted benzene ring.

Aromatic multiplet signals within $7.15\text{-}8.09$ ppm registered in the corresponding NMR spectra. Two dublets at $5.10\text{-}5.12$ ppm and $6.12\text{-}6.20$ ppm were also observed (Table 2). MNR data also showed the sulfones as reaction products represented a mixture of two stereoisomers.

REFERENCES

1. Drabowicz J., Kielbasinski P., Mikolajczyk M. In S.Patai (Ed.), The Chemistry of Sulfinic Acids, Esters, and Derivatives; Wiley: New York, 1990, 12, 370.
2. Ogata Y., Sawaki Y., Isono M., Tetrahedron, 1969, 25, 2715.

Table 1. Physical and analytical data for compounds

Compound	Yield (%)	Tm (°C)	Molecular Formula	Molar mass (g.mol ⁻¹)	Analysis calc. (found)(%)			
					C	H	N	S
3a	92	137	C ₁₄ H ₁₁ FCINO ₄ S	342.5	49.05 (48.96)	3.21 (3.18)	4.09 (4.06)	9.34 (9.33)
3b	98	146	C ₁₅ H ₁₃ FCINO ₄ S	357.5	50.35 (50.31)	3.64 (3.62)	3.92 (3.91)	8.95 (8.94)
3c	96	151.5	C ₁₄ H ₁₀ FCINO ₄ S	378.0	44.44 (44.40)	2.65 (2.63)	3.78 (3.77)	8.46 (8.45)
3d	94	155	C ₁₄ H ₁₀ ClFBrNO ₄ S	422.5	39.75 (39.74)	2.86 (2.83)	3.31 (3.30)	7.51 (7.50)
3e	93	162	C ₁₄ H ₁₀ ClFJNO ₄ S	437.5	38.40 (38.38)	2.30 (2.27)	3.20 (3.18)	7.31 (7.30)
3f	97	149	C ₁₄ H ₁₀ FCIN ₂ O ₆ S	388.5	43.24 (43.22)	2.57 (2.55)	7.28 (7.26)	8.24 (8.23)
3g	96	159	C ₁₈ H ₁₃ FCINO ₄ S	393.5	54.89 (54.88)	3.37 (3.36)	3.56 (3.50)	8.13 (8.12)
3h	95	157	C ₁₆ H ₁₄ FCIN ₂ O ₅ S	400.5	47.94 (47.92)	3.50 (3.49)	5.99 (5.97)	7.99 (7.96)

Table 2. Spectroscopic data for compounds

Compound	IR data ν (cm^{-1})	$^1\text{H-NMR}$ (CDCl_3) δ (ppm)
3a	1565-1350 (NO_2) 1320-1135 (SO_2)	7.25-7.80 (m, 9H); 5.12 (d, CH); 6.20 (d, CH)
3b	1555-1340 (NO_2) 1325-1140 (SO_2)	7.26-7.82 (m, 8H); 5.10 (d, CH); 6.20 (d, CH)
3c	1560-1340 (NO_2) 1320-1140 (SO_2)	7.22-7.83 (m, 8H); 5.12 (d, CH); 6.18 (d, CH)
3d	1555-1330 (NO_2) 1325-1130 (SO_2)	7.20-7.88 (m, 8H); 5.15 (d, CH); 6.20 (d, CH)
3e	1560-1340 (NO_2) 1320-1130 (SO_2)	7.18-7.78 (m, 8H); 5.10 (d, CH); 6.18 (d, CH)
3f	1560-1350 (NO_2) 1330-1140 (SO_2)	7.20-7.80 (m, 8H); 5.10 (d, CH); 6.15 (d, CH)
3g	1565-1350 (NO_2) 1325-1140 (SO_2)	7.15-8.09 (m, 11H); 5.12 (d, CH); 6.12 (d, CH)
3h	1560-1345 (NO_2) 1330-1140 (SO_2)	7.25-7.88 (m, 8H); 5.10 (d, CH); 6.15 (d, CH)