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THE NUCLEOPHILIC SUBSTITUTION REACTION OF SULFINIC ACIDS WITH HALONITROALKANES

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ABSRACT

Arylsulfonylnitromethanes were obtained by nucleophilic substitution reaction. The suggested method of obtaining arylsulfonylnitromethanes 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. The structure of the new products were confirmed by ^{1}H NMR, IR and elemental analysis.

Key words: *arylsulfonylnitromethanes, synthesis, structure.*

INTRODUCTION

α – Nitrosulfones were obtained by the oxidation of α – nitrosulphides[1], an interaction between sulfonylcarbanion and organic nitrate, or a reaction of metal sulfides and sulfinic acids with α – chloro-, α – bromo-, α

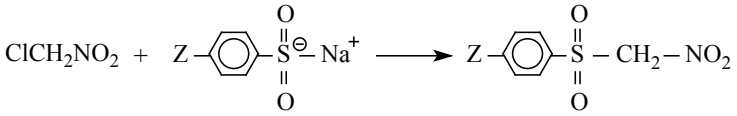
– iodonitroalkanes[2]. In one particular case alone, a direct nitration of arylsulfone was made resulting in α – nitrosulfone. Zeilstra *et al* suggested a method of obtaining α – nitrosulfones based on the reaction between potassium nitronate and p-toluene sulfonylbromide[3]. Publications describing a method of obtaining α – nitrosulfones by nitration in the presence of bases are also available. Studies on the chemical behaviour of α – nitrosulfones show that they readily take part in reactions of nucleophilic addition[2]. As a result, α – nitroesters, nitroacetonitriles, bis(phenylsulfonyl)methane and bis(alkylsulfonyl)methanes are obtained. They react readily with aldehydes, and alcohols, alkenes or bisaducts are obtained. Arylnitromethylethylsulfones can also be used to obtained bis(arylsulfonyl)furans[5]. Wade *et al* found out that phenylsulfonylnitromethane takes part in C-alkylation reacton resulting in a series of α – nitrosulfones. Studies on the conformation of aromatic α – nitrosulfones were also made[4].

The present work proposes a original method of obtaining arylsulfonylnitromethanes.

Structure of the new compounds were eluci dated on the basis of elemental analysis and spectral data.

RESULTS AND DISCUSSION

Arylsulfonylnitromethanes were obtained by a nucleophilic substitution reaction.



Z = H (1); Z = 4-Me (2); Z = 4-MeO (3);
Z = 4- Cl (4); Z = 4-Br (5); Z = 4-I (6).

Scheme 1.

The suggested method of obtaining arylsulfonylnitromethanes has some important advantages over the methods known 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.

Arylsulfonylnitromethanes 1–6 were synthesized by mixing equimolar quantities of the corresponding reagents in ethanol at 18–20 ºC from 12 to 72 hours. These compounds are colourless, crystalline substances, very soluble in chloroform, acetone and dioxane. They are stable for long storage periods and melt without decomposing. The compounds obtained were identified by TLC.

All the products 1–6 were purified by recrystalization or flash column chromatography on silica gel with a benzene as the eluent. The structure of compounds 1–6 confirmed by ^{1}H – and ^{13}C-NMR, IR spectra, and elemental analysis (Table 1, 2).

Table 1. *Characterization Data of the New Synthesized Compounds*

Comp. №	Mp., ºC (solvent)	Color Yield %	Mol. formula mol.wt	Calcd. / found %			
				C	H	N	S
1	76–77 (EtOH)	White 81	$C_7H_7NO_4S$ (201.14)	43.60 43.54	3.71 3.68	7.06 6.98	15.60 15.53
2	73–74 (EtOH)	White 78	$C_8H_9NO_4S$ (215.16)	44.20 44.15	3.95 3.89	6.72 6.66	14.58 14.49
3	79–80 (EtOH)	White 75	$C_8H_9NO_5S$ (231.13)	41.57 41.53	3.65 3.59	5.80 5.73	13.95 13.90
4	138–139 (EtOH/ Dioxane)	White 82	$C_7H_6ClNO_4S$ (235.58)	35.55 35.49	2.40 2.35	5.76 5.70	13.45 13.39
5	159 (EtOH/ Dioxane)	White 74	$C_7H_6BrNO_4S$ (280.12)	29.75 29.73	2.45 2.40	5.38 5.32	11.65 11.61
6	186–187 (EtOH/ Dioxane)	White 86	$C_7H_6INO_4S$ (327.03)	25.50 25.43	1.56 1.50	4.38 4.33	9.70 9.67

Table 2. *Spectral Data of Some New Synthesized Compounds*

Comp. №	Spectral Data
1	^{1}H NMR (δ, ppm): 5.52 (d, J = 5.8 Hz, 2H), 7.24 – 7.80 (m, 5H); ^{13}C (δ, ppm): 32 (methylene), 131 (Ar-C); IR(υ, cm^{-1}): 1550, 1340 (NO_2), 1310, 1150 (SO_2), 2930, 2850, 1450 (CH_2).
2	^{1}H NMR (δ, ppm): 2.42 (s, CH_3), 5.50 (d, J = 5.6 Hz, 2H), 7.20 – 7.85 (m, 4H); ^{13}C (δ, ppm): 33.2 (methylene), 130 (Ar-C); IR(υ, cm^{-1}): 1545, 1345 (NO_2), 1305, 1140 (SO_2), 2920, 2845, 1450 (CH_2).

3	^{1}H NMR (δ, ppm): 2.40 (s, CH_3), 5.51 (d, J = 5.6 Hz, 2H), 7.25 – 7.75 (m, 4H); ^{13}C (δ, ppm): 32.4 (methylene), 131 (Ar-C); IR(υ, cm^{-1}): 1550, 1340 (NO_2), 1310, 1145 (SO_2) 2920, 2845, 1470 (CH_2).
4	^{1}H NMR (δ, ppm): 5.53 (d, J = 5.8 Hz, 2H), 7.20 – 7.85 (m, 4H); ^{13}C (δ, ppm): 32.6 (methylene), 130 (Ar-C); IR (υ, cm-^{1}): 1560, 1345 (NO_2), 1305, 1150 (SO_2), 2925, 2855, 1455 (CH_2).
5	^{1}H NMR (δ, ppm) 5.51 (d, J = 5.8 Hz, 2H), 7.23 – 7.84 (m, 4H); ^{13}C (δ, ppm): 31.8 (methylene), 130 (Ar-C); IR(υ, cm^{-1}) 1555, 1340 (NO_2), 1300, 1140 (SO_2), 2930, 2860, 1460 (CH_2).
6	^{1}H NMR(δ, ppm): 5.52 (d, J = 5.8 Hz, 2H), 7.20 – 7.78 (m, 4H); ^{13}C (δ, ppm): 32.2 (methylene), 131 (Ar-C); IR(υ, cm^{-1}): 1550, 1335 (NO_2), 1305, 1145 (SO_2), 2920, 2850, 1460 (CH_2).

The ^{1}H(^{13}C) –NMR spectra of arylsulfonylnitromethanes contain an aromatic multiplet at 7.24 – 7.85 (130–131) ppm. The shifts of methylene protons can be seen at 5.50 – 5.53 (31.4–33.2) ppm. The chemical shift of the methyl group in the benzene nucleus is at 2.40 ppm. The presence of a methyl group does not effect substantially the position of the aromatic multiplet.

The IR spectra of the compounds obtained contain intensive absorption bands of nitro – and sulfonyl groups. Asymmetric and symmetric valence vibrations of nitro groups can be seen at 1560–1545 and 1345–1335 cm^{-1}, while the asymmetric and symmetric vibrations of sulfonyl group are at 1310–1300 and 1150–1140 cm^{-1}. These bands are highly intensive since the sulfonyl group are not situated on the same plane as the other substitutes. The absorption bands at 3100–3000 cm^{-1} are assigned to valence C-H aryl vibration. A triplet characterized by a decreasing intensity of the high-frequency bands can be seen in this interval because the molecules of the compounds under study contain monosubstituted benzene nuclei. The skeleton vibrations of the arene nucleus at 1640–1600 and 1480–1450 cm^{-1}. There is an absorption band of a monosubstituted benzene nucleus at 700 cm^{-1}, and an absorption band of a p-disubstituted nucleus at 810–800 cm^{-1}. A characteristic band of valence C-N vibration can be seen at 850–840 cm^{-1}. The methylene group is identified by the absorption maximums of valence asymmetric and symmetric vibrations at 2930–2845 cm^{-1} and deformation

vibrations at 1470–1450 cm^{-1}. The absorbtion band of asymmetric and symmetric valence vibrations at 2950–2850 cm^{-1} is due to the methyl group in p-position in the arene nucleus. The presence of a methoxy group in the benzene nucleus is proved by the absorption bands of valence vibrations of the methyl group at 2840 cm^{-1} and the valence asymmetric and symmetric vibrations of C-O-C bond at 1270 and 1030 cm^{-1}. The presence of a halogen atom in the phenylsulfonyl group result in characteristic band at 800–580 cm^{-1}. An absorption band of medium intensity corresponding to valence S-aryl vibrations is characteristic of all arylsulfonylnitromethanes at 1090–1080 cm^{-1}.

CONCLUSIONS

There new compounds (3, 5, 6) were synthesized by means of S_{N^2} reaction. The obtained series of arylsulfonylnitromethanes are very important from preparative point of view since these compounds are active methylene components. Part of these compounds was tested antifungal activity and found that they are potential growth inhibitors causal fungal.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are uncorrected. The elemental analysis were carried out in the Microanalytical Center at University Prof. A. Zlatarov. The infrared spectra were recorded on a Specord spectrometer using KBr discs in the range 4000 to 400 cm^{-1}. ^{1}H-NMR (chemical shifts measured in deuterated solvent are given in ppm from TMS) spectra were recorded with a Bruker 250 MHz spectrometer, using $CDCl_3$ solution.

PREPARATION OF 1 – 6

An equimolar quantity of chloronitromethane dissolved in ethanol (25 ml) was added to the sodium salt of sulfinic acid (0,01 mol). The reaction mixture was rapidly stirred and then allowed to stay from 12 to 72 hours at a room temperature. The crystals obtained were separed from the reaction mixture and were recrystallized from ethanol and ethanol/dioxane.

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