STUDY ON THE REACTION OF 2-BROMO (CHLORO)-2-NITROETHENYLARENES AND THIOLATE IONS

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ABSTRACT

The nucleophilic addition reactions of both the thiolate ions whit β-bromo-β-nitrostyrene derivatives have been studied. The structure of halonitrosulfides thus obtained were confirmed by microanalytical and spectral methods.

***Key words**: S-containing nucleophile, nitrosulfides, nucleophilic addition*

INTRODUCTION

A number of publications dealing with the addition of S-containing nucleophiles [1-2]. Nucleophilic addition reactions are convenient and selective method of establishing a linkage C-S. The production of sulfides is a practical reaction as these compounds have proven antifungal activity.

The aim of the presence study was examine the structural characteristic of series of sulfides prepared by known method under midl conditions.

MATERIALS AND METHODS

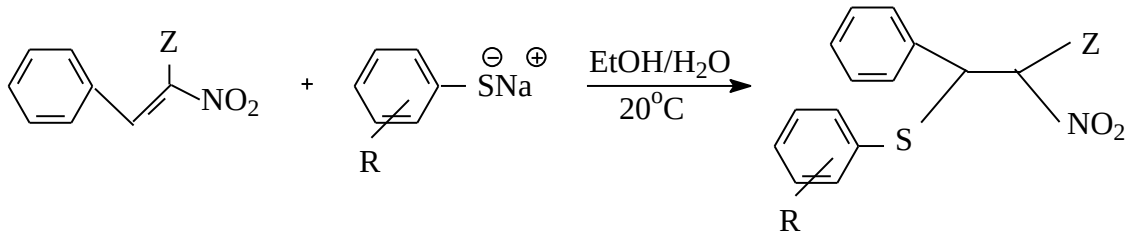
General remarks. Thiophenol, 4-methyl- and 4-nitrothiophenol are commercial products of Aldrich Chemical Compony, Inc. β-Bromo –and β-chloro-β-nitrostyrene were obtained by corresponding literature [3]. The composition and structure of the sulfides were confirmed by elemental microanalysis and different spectral methods.

Apparatus. Elemental microanalyses of the compounds studied were performed using Carlo Erba unstrument (Italy). Infrared spectra were recorded with a Bruker spectrophotometer. The samples were prepared as KBr pellets. Melting points are unccorected.

General procedure for preparation of compounds 3a-f. 0.01 mol of the corresponding S-containing nucleophiles, dissolved in a minimum amount of water, was added to a solution of 0.01 mol β- bromo (β-chloro-) β-nitrostyrene in 10 ml ethanol and the mixture kept for 8 h. The crystalline products obtained were filtered and purified by recrystallization from benzene/dioxane. The produts were found to be stable on prolonged storage in air and were soluble in acetone, but insoluble in chloroform and petroleum ether.

RESULTS AND DISCUSSION

The interaction of thiolate ions with β-bromo (chloro)-β-nitrostyrene occurs according to the reactions depicted in Scheme 1.



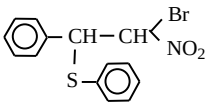
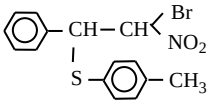
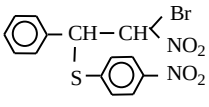
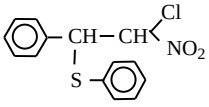
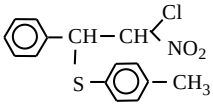
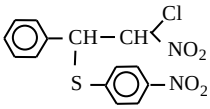
3 a-f

3a(Br, R=H); 3b(Br, R=4-Me);
3c(Br, R=4-NO_2); 3d(Cl, R=H);
3l(Cl, R=4-Me)
3f(Cl, R=4-NO_2)

Sulfides 3a-f are synthesized as results of the reaction of equimolar amounts of the corresponding reagents in medium in ethanol/water at room temperature for 8h. The crystalline products obtained were filtered. The products were found to be stable on prolonged storage in air and were soluble in ethanol. The yields obtained varied the range 84-92%.

IR-spectra of the compounds studied display strong absorption bands, characteristic for NO_2 functional group. Medium-intensity absorption bands at 1090-1080 cm^{-1} could be assigned to stretching S-aryl vibration. The band at 855-845 cm^{-1} could be assigned to stretching C- N vibration. Skeletal vibration 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.

Physical and analytical data

Compound	Yield (%)	Tm (^oC)	Molecular Formula Molar mass ($g.mol^{-1}$)	Analysis calc. (found)(%)				IR-data (KBr) $\nu(cm^{-1})$
				C	H	N	S	
	89	132	$C_{14}H_{12}BrNO_2S$ (338)	49.59 (49.70)	3.49 (3.55)	9.40 (9.47)	4.07 (4.14)	1560, 1350(NO_2); 1080(Ar-S)
	86	141	$C_{15}H_{14}BrNO_2S$ (352)	51.06 (51.14)	3.92 (3.98)	3.95 (3.98)	9.03 (9.09)	1560, 1355(NO_2); 1080(Ar-S)
	91	147	$C_{14}H_{11}BrN_2O_4S$ (383)	43.86 (43.82)	2.87 (2.81)	7.31 (7.21)	8.36 (8.30)	1555, 1355(NO_2); 1085(Ar-S)
	84	129	$C_{14}H_{12}ClNO_2S$ (293.5)	57.17 (57.24)	4.06 (4.09)	4.70 (4.77)	10.72 (10.93)	1552, 1353(NO_2); 1080(Ar-S)
	86	135	$C_{15}H_{14}ClNO_2S$ (307.5)	58.47 (58.54)	4.49 (4.55)	4.50 (4.52)	10.40 (10.41)	1560, 1350(NO_2); 1090(Ar-S)
	92	142	$C_{14}H_{11}ClN_2O_4S$ (338.5)	49.59 (49.63)	3.20 (3.25)	8.22 (8.27)	9.43 (9.45)	1560, 1355(NO_2); 1090(Ar-S)

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