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RESEARCH ARTICLE

Nucleophilic reactions of ethylene derivatives. I. Reaction of α-iodo-β-nitrostyrene with sulfinic acids

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1-Aryl-1-arylsulfonylethene derivatives have been prepared by the interaction of α-iodo-β-nitrostyrene with arenesulfinic acids. The structure of the products were confirmed by ^{1}H-NMR, IR, UV spectroscopy and elemental analysis. The kinetic studies indicated that the reaction took place via vinyl nucleophilic substitution mechanism. The principal kinetics and reaction parameters were determined.

Keywords: α-iodo-β-nitrostyrene; sulfinic acids; S_NVIN-reaction

1. Introduction

β-Nitrostyrene and its halogenated derivatives such as bromostyrenes are known to have functional activity. The genotoxicity of these compounds was studied, employing *Salmonella typhimurium* strains (*1*). *Schales* and *Graefe* have reported on the anti-bacterial activity of 4-bromo-*ω*-nitrostyrene and 4-iodo-*ω*-nitrostyrene with respect to *Staphylococcus aurea* (*2*). This prompted the development of novel, more facile methods for the preparation of nitrostyrene and its derivatives (*3, 4*), as well as studies on their π-diastereomers (*5*) and chemical reactivities (*6–9*).

Vinyl nucleophilic substitution (S_NVIN) was studied in detail for halonitrostyrenes and the rate constants as well as activation parameters were determined. Moreover, stereochemistry of the corresponding reactions was studied. Based on these results, the most probable mechanisms of the S_NVIN reactions for the reactions of various halonitrostyrenes with nitrogen-, oxygen-, and sulfur-containing nucleophiles were suggested (*9–15*).

No data, however, have been reported in the literature so far, concerning the interactions between α-iodo-β-nitrostyrene and sulfinic acids. Therefore, the objective of the present work was the synthesis of some novel vinylsulfones as well as studies on the mechanism of the corresponding reactions, involving these substrates.

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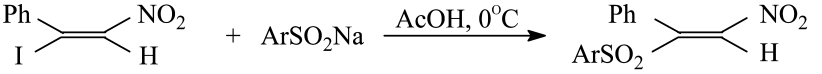
2. Results and discussion

2.1. *Synthesis*

1-Aryl-1-arylsulfonyl-2-nitroethenes were synthesized by the reaction of equimolar amounts of α-iodo-β-nitrostyrene and sodium salt of sulfinic acid in the presence of acetic acid at 0 °C for 30 min (Scheme 1).



1 Z - or E - 2 3 Z - or E -

Ar = Ph (2a, 3a); Ar = 4-MeC_6H_4 (2b, 3b); Ar = 4-ClC_6H_4 (2c, 3c);
Ar = 4- BrC_6H_4 (2d, 3d); Ar = 4- $AcNHC_6H_4$ (2e, 3e); Ar = 2-$C_{10}H_7$ (2f, 3f)

Scheme 1.

The chemical composition and structure of the synthesized compounds were comfirmed by analytical and spectral methods (Tables 1 and 2).

The IR spectra of 1-aryl-1-arylsulfonyl-2-nitroethenes contain intensive absorption bands of asymmetric and symmetric valence vibration of a nitrogroup at 1545–1505 and 1360–1335 cm^{-1}, and sulfophenyl group at 1320–1315 cm^{-1}, 1150–1140 cm^{-1}. The absorption maximum at 890–850 cm^{-1} confirms the presence of a triple–substituted double bond. Absorption bond corresponding to valence C−H aryl vibration can be seen at 3080–3000 cm^{-1} (a triplet). The skeletion vibrations of the aromatic nucleus give rise to absorption maxima at 1630–1600, 1500–1490 and 1450–1400 cm^{-1}. In some cases, the band at 1600 cm^{-1} is a doublet with a second maximum at 1580 cm^{-1} resulting from conjugation of the benzene nucleus. C−H-Aryl off plane deformation vibrations at 820–790 cm^{-1} prove the presence of a p-substituted benzenes.

The ^1H NMR spectra of 1-aryl-1-arylsulfonyl-2-nitroethenes contain shifts of aromatic multiplets in a comparatively wide range 7.20–7.95 ppm. The shifts for the aromatic protons teng to shift towards a weaker fieled and so does the shift for the vinyl proton since the carbon atoms are bound to acceptor substituents.

Table 1. Analytical and spectral data for compounds 3a–f.

Compound No	Yield %	m.p. °C	Formula m. wt.	Analysis (%) found (calc.) C	H	N	S
3a	90	112	$C_{14}H_{11}NO_4S$ 299.22	58.36 (58.13)	3.82 (3.81)	4.75 (4.84)	11.26 (11.07)
3b	79	117	$C_{15}H_{13}NO_4S$ 303.24	59.63 (59.41)	4.49 (4.29)	4.66 (4.62)	10.84 (10.56)
3c	68	109	$C_{14}H_{10}ClNO_4S$ 333.68	51.81 (51.93)	2.86 (3.09)	4.07 (4.33)	9.93 (9.89)
3d	50	105	$C_{14}H_{10}BrNO_4S$ 358.23	45.70 (45.65)	2.59 (2.72)	3.54 (3.80)	8.47 (8.69)
3e	65	171	$C_{16}H_{14}N_2O_5S$ 342.25	55.60 (55.50)	4.04 (4.05)	8.03 (8.09)	9.55 (9.25)
3f	52	125	$C_{18}H_{11}NO_4S$ 437.27	64.17 (64.09)	3.55 (3.26)	4.02 (4.15)	9.88 (9.50)

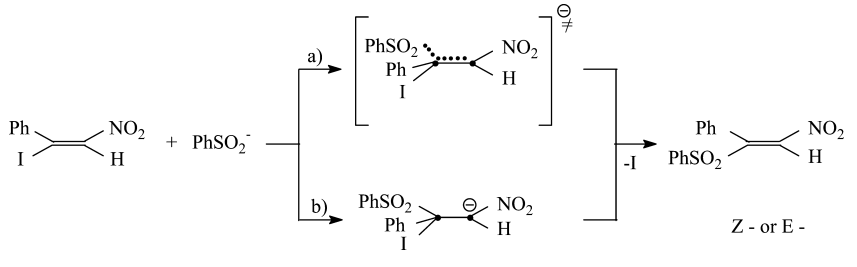
Table 2. Spectral data of the compounds 3a-f.

Compound No	IR (ν, cm^{-1}) KBr	UV/VIS (EtOH) λ max (nm) (lgε)	^{1}H -NMR (δ, ppm, $CDCl_3$)
3a	1520, 1350 (NO_2); 1320, 1150 (SO_2); 1080 (Ph–S); 850 (=CH)	211 (2.54); 258 (3.08); 271 (2.95)	7.25–7.81 (10H, m); 8.01 (S, =CH)
3b	1520, 1345 (NO_2); 1320, 1145 (SO_2); 1080 (Ar–S); 850 (=CH)	210 (2.48); 269 (3.12); 270 (2.80)	2.43 (S, CH_3, 3H); 7.20–7.28 (m, 5H); 7.70–7.84 (m, 4H); 8.01 (S, =CH)
3c	1520, 1360 (NO_2); 1320, 1145 (SO_2); 1080 (Ar–S); 870 (=CH)	212 (2.50); 256 (2.98); 285 (2.81)	7.26–7.40 (m, 5H); 7.76 – 7.89 (m, 4H); 8.03 (S, =CH)
3d	1520, 1350 (NO_2); 1320, 1145 (SO_2); 1060 (Ar–S); 890 (=CH)	210 (2.38); 254 (2.90); 292 (2.69)	7.21–7.27 (m, 5H); 7.72 – 7.85 (m, 4H); 8.09 (S, =CH)
3e	1505, 1335 (NO_2); 1315, 1140 (SO_2); 1080 (Ar–S); 890 (=CH)	210 (2.20); 225 (3.21); 297 (2.50); 310 (2.45), 340 (2.12)	2.42 (S, CH_3, 3H); 7.20–7.28 (m, 5H); 7.70–7.86(m, 4H); 8.07 (S, =CH)
3f	1545, 1350 (NO_2); 1320, 1145 (SO_2); 1075 (Ar–S); 870 (=CH)	210 (2.35); 259 (3.15); 282 (2.75)	7.20–7.25 (m, 5H); 7.78 – 7.95 (m, 7H); 8.16 (S, =CH)

The UV spectra of the synthesized compounds show that the polarization of the double bond is inessential because of the centrofugal effect of the sulfophenyl- and nitrogroup.

2.2. *Kinetic study*

The reaction of α-iodo-β-nitrostyrene and benzenesulfinic acid can proceed, according to two principal mechanisms: (a) synchronic formation of C–Nu bond and C–X bond scission; and (b) addition-elimination with the formation of carbenium ion as an intermediate (Scheme 2).

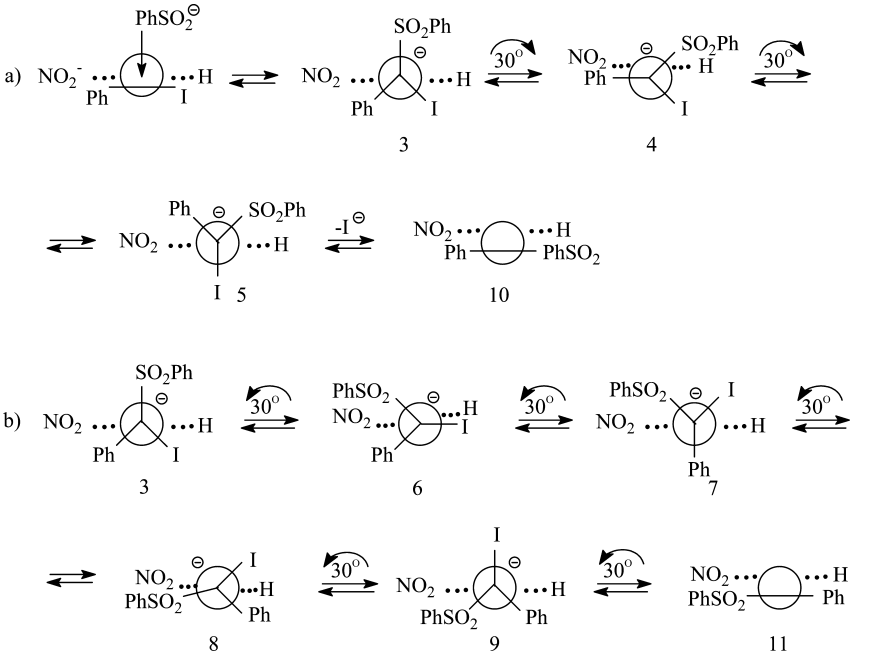


Scheme 2.

Since the nucleophile carries negative charge, the S_NVIN takes place in accordance with mechanism (b). The carbanion formed after the nucleophilic attack has its negative charge on the β-carbon and therefore, $k_{rot} > k_{el}$.

Scheme 3 shows the mechanism of the S_NVIN reaction, characterized by the formation of products 10–11 from carbanion (3).

Product 10 was formed by clockwise rotation at 60° with respect to C_α–C_β (3 → 4 → 5). Counterclockwise rotation at 120°(3 → 6 → 7 → 8 → 9) was accompanied by shift of the leaving group and resulted in the formation of product 11 with reversal in the molecular configuration.



Scheme 3.

Table 3. Coefficient and activation parameters for the reaction of α-iodo-β-nitrostyrene with benzenesulfinic acid in ethanol.

α-iodo-β-nitrostyrene	10^2 K ($M^{-1}s^{-1}$)			(kJ/mol) Ea	$\Delta S^{\pm}$ (O°) (e.u.)
	0°	15°	25°		
	1.55	6.27	14.18	22.4	−7.0

Note: Probable errors are 2% for K; ± 0.5 kJ/mol for Ea, and 1.5 e.u. for $\Delta S^{\pm}$.

To establish whether the reaction was kinetically or thermodynamically controlled, the isomeric compositions of both the α-iodo-β-nitrostyrene starting material and final product of nucleophilic substitution were determined. The Z/E diaseteromeric ratio for α-iodo-β-nitrostyrene was found to be 2:1. The isomeric composition for the product of the nucleophilic substitution also favored the Z-isomer formation ($Z/E = 2.5 : 1$). Significant amount of non-reacted α-iodo-β-nitrostyrene, mostly E-isomer, was found to exist in the reaction mixture. Therefore, Z-isomer possessed higher reactivity, due to an enhanced steric strain. Bearing in mind the intramolecular effects of the sulfur and the experimental results, it becomes clear that the reaction of benzenesulfinic acid and α-iodo-β-nitrostyrene is kinetically controlled (Table 3) with preservation of the molecular configuration.

3. Experimental

3.1. *Methods*

Melting points were determined on a Melt-Temp apparatus and are uncorrected. Mycroanalyses were obtained using an elemental Analyser (Carlo-Erba), IR- and UV-spectra were obtained using

a Bruker and Specord UV–VIS. ^{1}H-NMR (chemical shifts measured in deuterated solvents are given in ppm from TMS) spectra were recorded a Bruker 250 MHz spectrometer, using $CDCl_3$ solution.

3.2. *Materials*

α-Iodo-β-nitrostyrene and sulfinic acids were prepared and purified as described in the literature (*16, 17*).

3.3. *Synthesis of 1-aryl-1-arylsulfonyl-2-nitroethenes*

To 0.001 mol of sodium benzenesulfinate dissolved in 5 ml water, 0.001 mol acetic acid and 0.001 mol α-iodo-β-nitrostyrene, dissolved in 5 ml ethanol were added. The reaction mixture was allowed to stand for 30 min at temperature of 0 °C. The nitrosulfones thus obtained were subsequently filtered and re-crystallized from ether/hexane mixture.

3.4. *Rate measurements*

Purified sulfinic acid (0.001 mol) were added to α-iodo-β-nitrostyrene (0.001 mol) in ethanol (50 ml). Aliquots were taken out the regular intervals of time and diluted with ethanol. The flow concentration of th reagents during the reaction were determined by UV-spectrophotometry.

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