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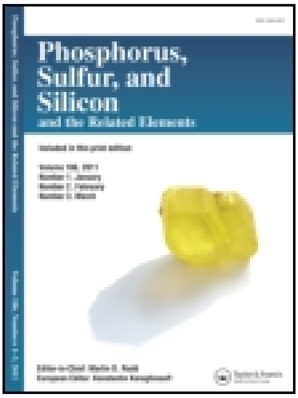

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REACTION OF SULFINIC ACIDS WITH HETEROCONJUGATED ALKENES

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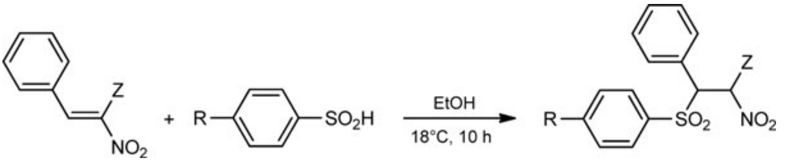
GRAPHICAL ABSTRACT



Abstract *The nucleophilic addition reactions of arenesulfinic acids with heteroconjugated alkenes have been studied. The structures of the sulfones thus obtained were confirmed by microanalytical and spectral methods. Kinetic parameters of the nucleophilic addition reactions were determined. Interactions are second-order reactions, but they are first order regarding each reagent. The influence of various substituents at the carbon–carbon double bond on the nucleophilic activity was studied.*

Keywords Heteroconjugated alkenes; nucleophilic addition; sulfinic acids

INTRODUCTION

Heteroconjugated alkenes containing electron-withdrawing functional groups ($COCH_3$, $CONH_2$, $COOCH_3$, CN, SO_2CH_3, NO_2, etc.) are highly reactive compounds. Sulfinic acids act mostly as *S*-nucleophiles rather than *O*-nucleophiles because of the presence of an electron pair at the sulfur atom.[1] The addition of sulfinic acids to α,β-unsaturated compounds is known to result in the formation of β-nitro-, keto-, cyano-, etc. sulfones.[2–8] The high reactivity of functionalized alkenes corresponds to their high polarity and functionality; hence, they participate as reactants in similar noncatalytic reactions. On the other hand, heteroconjugated nitroalkenes represent a special group of Michael acceptors, which is due to the additional effect exerted by the nitro group on the reactivity of the unsaturated system.

The present work extends this reaction to the synthesis of new polyfunctional sulfones, and additionally, kinetic parameters of the nucleophilic addition reactions were determined.

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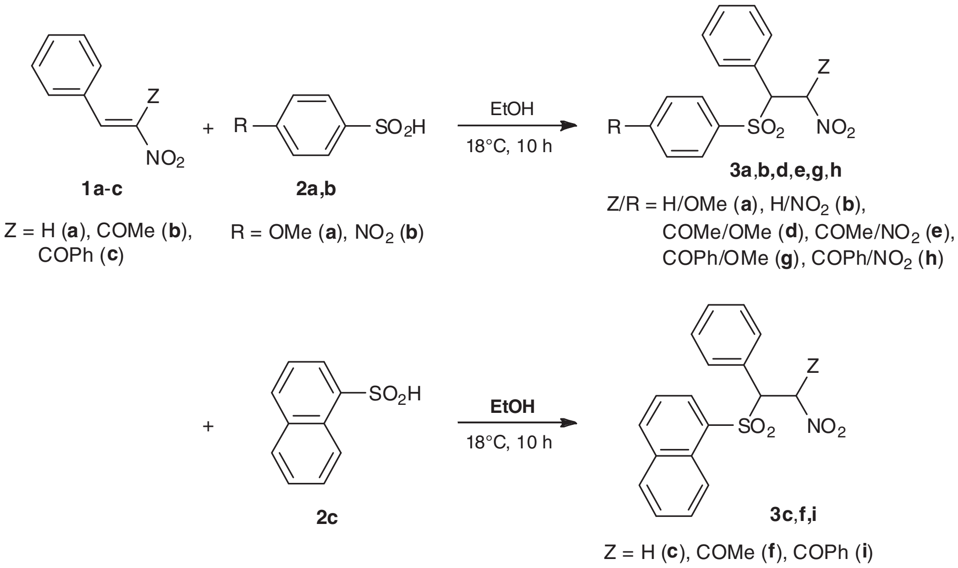

Scheme 1

Moreover, the kinetic studies allow an evaluation of the activity of the carbon–carbon double bond in the conjugated alkenes.

RESULTS AND DISCUSSION

The interaction of arenesulfinic acids **2a–c** with α,β-unsaturated compounds **1a–c** occurs according to the reactions depicted in Scheme 1.

Sulfones **3** are synthesized as results of the interaction of equimolar amounts of the corresponding reagents in ethanol at room temperature for 10 h. IR-spectra of the compounds studied display strong absorption bands, characteristic for both the NO_2 and SO_2 functional groups. Moreover, a trend toward an increase of the frequencies of the symmetric stretches for the NO_2 group was observed. No significant changes in this respect were found for the SO_2 group. The high intensities of these characteristic bands should be expected, having in mind the geometry of the SO_2 group with its out-of-plane location with respect to the other substituent. The IR-spectra of these particular organosulfur compounds show clearly that the SO_2 group cannot be considered as analogous to the carbonyl group, due to the differences in the symmetry and the electron structure. The spectral studies did not reveal any existence of conjugation between the SO_2 and NO_2 groups, which should be expected from their location at different planes. The absorption bands for the carbonyl groups were observed at 1705–1695 cm^{-1}. 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 vibrations, corresponding to three neighboring hydrogen atoms in the β-$SO_2C_{10}H_7$ group, were observed at 810–785 cm^{-1}.

Skeletal vibrations of the benzene ring were characterized by the bands at 1640–1450 cm^{-1}, and out-of-plane C—H aryl vibration within 725–720 and 830–790 cm^{-1} proved the presence of monosubstituted and disubstituted benzene ring, respectively. The presence of the *p*-methoxy group in the benzene ring was proved by the characteristic stretching vibration of the CH_3-group in methyl phenyl esters at 2845 cm^{-1}, and also by the bands at 1275 and 1025 cm^{-1}, corresponding to C—O—C fragment.

In the ^1H NMR spectra, multiplets characteristic for the aromatic protons are observed in the region of 7.00–7.80 ppm. The corresponding ^{13}C NMR signals appear at 128–135 ppm. In the case of **3a–c**, the protons of the ethane unit appear as doublet at 5.14–5.18 ppm and triplet at 6.18–6.21 ppm with a coupling constant of about 14 Hz. The corresponding ^{13}C NMR signals are found at 25–30 ppm and at 38–45 ppm, respectively. The NMR data also show that the sulfones are formed as a mixture of two stereoisomers.

The main kinetic parameters of the nucleophilic addition of sulfinic acids **2a**,**b** to nitroalkenes **1a–c** were determined by HPLC. This method was suggested by Aleksiev and Ivanova.[9] and modified by us to determine the kinetic parameters of the reaction. In all cases, the reactions were second order, but they were first order regarding the substrate and the nucleophilic reagent. The calculations were made by differential and integral methods in a wide concentration range 0.05–10 M. The results obtained were worked out by regression analysis with a correlation coefficient greater than 0.98. These results are very close to linear dependences and satisfy a second-order kinetic equation. The exact experimental values of the reaction order for the interaction between **1a** and **2a** (**2b**) were 1.69 (1.74) determined by Van't Hoff's method, and 1.79 (1.72) calculated by half-time method. The second-order rate constants for the addition of **2a** to **1a** at 288, 398, 308 K are 12.75 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 16.60 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 19.05 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, respectively. The rate constants of the reaction of **1a** with **2b** are 2.75 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 4.60 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 7.65 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1} ($T = 288, 398, 308$ K), respectively. The activation energy and the enthalpy of activation of the reaction of **1a** and **2a** were calculated to 47.26 and 45.50 kJ mol^{-1}, respectively. These results confirm the trend of the already observed nucleophilic activity of sulfinic acids depending on the substituent in the benzene ring. The activity of the nitroethylene system increases in the presence of COMe (COPh) group in α-position to NO_2: rate constants are 10.09 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 25.50 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 49.70 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1} ($T = 288, 398, 308$ K) for nucleophilic addition of **2a** to **1b** and 5.15 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 16.30 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1}, 42.70 ($\pm$0.1) $\times$ 10^{-4} M^{-1} s^{-1} for the interaction between **1c** and **2a**.

CONCLUSIONS

1. A new series of nitro- and ketosulfones was synthesized by the nucleophilic addition of sulfinic acids to heteroconjugated alkenes.
2. The reactivity of nitrochalcones correlates with that of nitroethenyl arenes in nucleophilic addition reactions.
3. The nucleophilic activity of sulfinic acids increases with the introduction of electron-donating substituents and decreases in the presence of electron-withdrawing substituents.

EXPERIMENTAL

Methods

Melting points are uncorrected. IR spectra (KBr) were recorded with a Bruker spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker (350 MHz) spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Chemical shifts are reported as δ

values. Microanalytical data were obtained using an elemental Analizer-1104 (Carlo–Erba). Selected physical and spectroscopic characteristics for synthesized compounds are given below. HPLC was performed using a Series-4 apparatus (Perkin–Elmer) and a programmable multiwavelength detector.

Synthesis of Compounds 3a–i: General Procedure

To the nitroalkene (0.1 mol) in 95% ethanol was added the corresponding sulfinic acid (0.1 mol). The reaction mixture was kept standing at 18 °C for 10 h. The crystalline products obtained were filtered and purified by recrystallization from dioxane/toluene. The products were found to be stable on prolonged storage in air and were soluble in acetone and chloroform but resulted insoluble in water, *n*-hexane and petroleum ether. The yields obtained varied within the range 93%–98%.

3a: Yield 93%; colorless crystals; mp 166 °C; IR (KBr, cm^{-1}) υ: 1550, 1360 (NO_2), 1305, 1140 (SO_2); ^1H NMR ($CDCl_3$) δ: 7.20–7.75 (m, 9H, arom-H), 5.15 (d, $J_{HH} = 14.2$ Hz, 1H, CH), 6.20 (t, $J_{HH} = 14.2$ Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ: 26.2, 28.2 (CH_2), 41.3 (CH), 129.6–147.3 (Ar-C). Calcd for $C_{15}H_{15}NO_5S$ (321.23): C, 56.07; H, 4.67; N, 4.36, S, 9.98%. Found: C, 56.00; H, 4.66; N, 4.34; S, 9.96%.

3b: Yield 96%; colorless crystals; mp 159 °C; IR (KBr, cm^{-1}) υ: 1555, 1360, (NO_2), 1360, 1140 (SO_2); ^1H NMR ($CDCl_3$) δ: 7.22–7.78 (m, 9H, arom-H), 5.16 (d, $J_{HH} = 14.2$ Hz, 1H, CH), 6.19 (t, $J_{HH} = 14.2$ Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ: 26.7, 29.1 (CH_2), 40.3 (CH), 128.6–150.7 (C-Ar). Calcd for $C_{14}H_{12}N_2O_6S$ (336.32): C, 50.00; H, 3.57; N, 8.37; S, 9.53%. Found: C, 49.93; H, 3.56; N, 8.37; S, 9.52%.

3c: Yield 95%; colorless crystals; mp 188 °C; IR (KBr, cm^{-1}) υ: 1560, 1365 (NO_2), 1310, 1140 (SO_2); ^1H NMR ($CDCl_3$) δ: 7.22–7.83 (m, 12H, arom-H), 5.15 (d, $J_{HH} =$ 13.9 Hz, 1H, CH), 6.19 (t, $J_{HH} = 13.9$ Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ: 25.2, 28.2 (CH_2), 40.4 (CH), 132.2–155.6 (C-Ar). Calcd for $C_{18}H_{15}NO_4S$ (405.29): C, 53.34, H, 3.71, N, 3.46, S, 7.91%. Found: C, 53.32; H, 3.69; N, 3.45; S, 7.90%.

3d: Yield 95%; colorless crystals; mp 156 °C; IR (KBr, cm^{-1}) υ: 1560, 1360 (NO_2), 1310, 1135 (SO_2), 1695 (CO); ^1H-NMR ($CDCl_3$) δ: 7.09–7.88 (m, 9H, arom-H), 5.12 (d, $J_{HH} = 14.1$ Hz, 1H, CH), 6.21 (d, $J_{HH} = 14.1$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 24.8, 26.2 (CH_2), 39.1 (CH), 129.3–153.8 (C-Ar). Calcd for $C_{17}H_{17}NO_6S$ (363.25): C, 56.21; H, 4.68; N, 3.86; S, 8.83%. Found: C, 56.20; H, 4.65; N, 3.85; S, 8.82%.

3e: Yield 95%; colorless crystals; mp 155 °C; IR (KBr, cm^{-1}) υ: 1560, 1360 (NO_2), 1310, 1140 (SO_2), 1695 (CO); ^1H NMR ($CDCl_3$) δ: 7.20–7.72 (m, 9H, arom-H), 5.16 (d, $J_{HH} = 14.1$ Hz, 1H, CH), 6.20 (d, $J_{HH} = 14.1$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 24.7, 27.5 (CH_2), 40.3 (CH), 128.2–158.9 (C-Ar). Calcd for $C_{16}H_{14}N_2O_7S$ (378.25): C, 50.81; H, 3.70; N, 7.41; S, 8.48%. Found: C, 50.80; H, 3.68; N, 7.40; S, 8.46%.

3f: Yield 97%; colorless crystals; mp 184 °C; IR (KBr, cm^{-1}) υ: 1560, 1355 (NO_2), 1310, 1140 (SO_2), 1695 (CO); ^1H NMR ($CDCl_3$) δ: 7.23–7.80 (m, 12H, arom-H), 5.15 (d, $J_{HH} = 14.0$ Hz, 1H, CH), 6.20 (d, $J_{HH} = 14.0$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 25.4, 27.8 (CH_2), 40.3 (CH), 131.2–159.3 (C-Ar). Calcd for $C_{20}H_{17}NO_5S$ (383.24): C, 62.68; H, 5.11; N, 3.65; S, 8.37%. Found: C, 62.66; H, 5.09; N, 3.62; S, 8.35%.

3g: Yield 96%; colorless crystals; mp 176 °C; IR (KBr, cm^{-1}) υ: 1560, 1355 (NO_2), 1310, 1140 (SO_2), 1705 (CO); ^1H NMR ($CDCl_3$) δ: 7.24–7.70 (m, 14H, arom-H), 5.15 (d, $J_{HH} = 14.1$ Hz, 1H, CH), 6.19 (d, $J_{HH} = 14.1$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 23.8, 25.9 (CH_2), 40.4 (CH), 130.2–152.8 (C-Ar). Calcd for $C_{22}H_{19}NO_6S$ (425.31): C, 62.13; H, 4.47; N, 3.29; S, 7.54%. Found: C, 62.11; H, 4.46; N, 3.27; S, 7.52%.

3h: Yield 98%; colorless crystals; mp 182 °C; IR (KBr, cm^{-1}) υ: 1560, 1360 (NO_2), 1310, 1140 (SO_2), 1705 (CO); ^1H NMR ($CDCl_3$) δ: 7.25–7.72 (m, 14H, arom-H), 5.16 (d, $J_{HH} = 14.0$ Hz, 1H, CH), 6.20 (d, $J_{HH} = 14.0$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 24.4, 26.7 (CH_2), 39.3 (CH), 129.4–156.6 (C-Ar). Calcd for $C_{21}H_{16}N_2O_7S$ (440.30): C, 57.29; H, 3.63; N, 6.39; S, 7.28%. Found: C, 57.28; H, 3.60; N, 6.37; S, 7.27%.

3i: Yield 98%; colorless crystals; mp 187 °C; IR (KBr, cm^{-1}) υ: 1560, 1355 (NO_2), 1310, 1140 (SO_2), 1705 (CO); ^1H NMR ($CDCl_3$) δ: 7.20–7.78 (m, 17H, arom-H), 5.16 (d, $J_{HH} = 14.0$ Hz, 1H, CH), 6.20 (d, $J_{HH} = 14.0$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 22.8, 25,1 (CH_2), 40.2 (CH), 130.2–157.6 (C-Ar). Calcd for $C_{25}H_{19}NO_5S$ (445.34): C, 67.98; H, 4.27; N, 3.14; S, 7.20%. Found: C, 67.96; H, 3.12; N, 3.12: S, 7.20%.

Rate Measurement

The purified sulfinic acid (0.001 mol) was added to the corresponding nitroalkene (0.001 mol) in ethanol (50 mL). Aliquots were taken out at regular intervals of time and diluted with ethanol. Flow concentration of nitroalkene during the reaction was determined by liquid chromatographic analysis. The experimental data obtained were consistent with a second-order kinetic equation yielding linear regression analysis with correlation coefficient 0.95, which proved the relevancy of the linear approximation.

The second-order constants, the activation energy, and enthalpy of activation were calculated according to known procedure.[10]

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