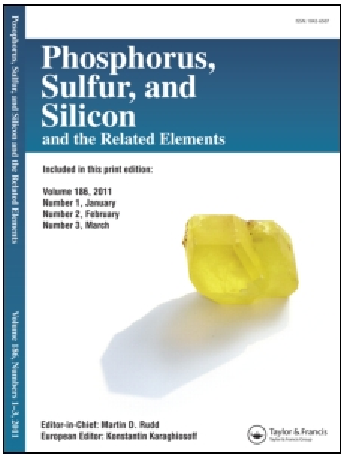

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Synthesis and Studies of Some Ketosulfones, Part II

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Synthesis and Studies of Some Ketosulfones, Part II

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Bromoketosulfones have been prepared. Their chemical composition and structure are proved by spectral methods. The addition of unsubstituted and substituted sulfinic acid to 2-bromo-1,3-diphenyl-2-propenone and 3-bromo-4-phenyl-3-butene-2-on has been studied kinetically by means of UV spectroscopy. Reactions follow the second-order kinetics V = R [bromochalkone][sulfinic acid]. The dependence of rate constants on the temperature and the influence of p-substitutents on the kinetic parameters have been investigated. The activation energy and the enthalpy of activation are calculated in the temperature range 288–308 K.

Keywords Bromochalkones; nucleophilic addition; sulfinic acids

INTRODUCTION

Literature reviews show that the processes of isomerization of chalkones, their physiological effect, and ways of extracting some of them from natural resources have already been studied thoroughly. A number of 2′-hydroxychalkones occur in nature. They constitute the primary precursors of all important natural flavonoids[1] and can be converted in the laboratory into other flavonoids and dihydrochalkones.[2] Chalkones have different physiological activities and act as antibiotics.[3] They find application in industries and as artificial sweetners.[4]

The present work aims at studying the nucleophilic addition of sulfinic acids to unsaturated bromochalkones. From a theoretical point of view, it is interesting to study the change in the activity of the carbon–carbon double bond regarding nucleophilic reagents depending simultaneously on a keto group and a halogen atom. On the other hand, the

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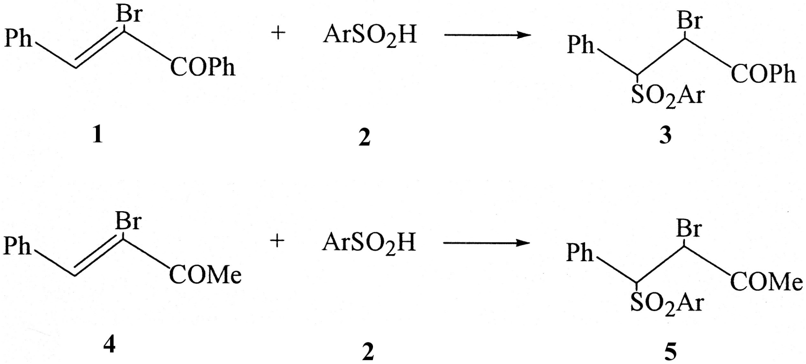
ketosulfones obtained are compounds having potential physiological properties, and this fact determines the importance of this study.

RESULTS AND DISCUSSION

Synthesis

The reaction between bromochalkones and arenesulfinic acids takes place by Scheme 1:



SCHEME 1 Ar = Ph (**2a**, **3a**, **5a**); Ar = 4-MeC$_6$H$_4$ (**2b**, **3b**, **5b**); Ar = 4-ClC$_6$H$_4$ (**2c**, **3c**, **5c**).

3-arylsulfonyl-2-bromo-1,3-diphenylpropanones (**3a–c**) and 4-arylsulfonyl-3-bromo-4-phenyl-2-butanones (**5a–c**) were synthesized as a result of the interaction of equimolar amounts of the corresponding reagents (**2a–c** reacts with **1** and **4**, respectively) in ethanol at r.t. for 24 h. The compounds obtained are colorless crystalline substances and are stable at long storage (Table I).

Spectroscopic Analysis

In the IR spectra of 3-arylsulfonyl-2-bromo-1,3-diphenylpropanones and 4-arylsulfonyl-3-bromo-4-phenyl-2-butanones, there are intensive absorption bands corresponding to the asymmetric and symmetric valence vibration of the sulfonyl group at 1313–1297 and 1140–1135 cm^{-1}. An absorption band assigned to the carbonyl group can be seen at 1750–1663 cm^{-1}. Skeleton vibrations of the aromatic nucleus are characterized by an absorption band at 1640–1450 cm^{-1}. C—H Aryl off-plane deformation vibrations at 830–790 cm^{-1} prove the presence of p-substituted benzenes. The characteristic absorption maxima at 1360–1340 and 1160–1150 cm^{-1} show that there are arylsulfonyl groups present in the compounds under study.

TABLE I Physical and Analytical Data for Compounds 3–5

Compound no.	Yield %	M.P. °C	Formula mol. wt.	Analysis (%) found (calcd.) C	H	S
3a	80	212	$C_{21}H_{17}O_3SBr$ 429.29	58.76 (58.50)	3.96 (3.45)	4.81 (4.60)
3b	91	206	$C_{22}H_{19}O_3SBr$ 443.30	59.61 (59.45)	4.29 (4.10)	7.23 (7.31)
3c	93	204	$C_{21}H_{16}O_3SClBr$ 463.75	54.39 (54.05)	3.45 (3.12)	6.91 (6.75)
5a	87	147	$C_{16}H_{15}O_3SBr$ 367.24	52.33 (51.90)	4.08 (3.75)	8.73 (8.52)
5b	86	131	$C_{17}H_{17}O_3SBr$ 381.25	53.56 (53.15)	4.46 (4.08)	8.41 (8.12)
5c	95	140	$C_{16}H_{14}O_3SClBr$ 401.69	47.84 (47.60)	3.49 (3.20)	7.98 (7.50)

The ^1H NMR spectra contain chemical shifts for aromatic multiplets at 7.28–8.10 ppm. There are also two doublets centered at 5.15–5.25 ppm and 6.20–6.30 ppm, and integrals show that each doublet corresponds to one proton. The singlet assigned to the methyl protons is at 2.42 ppm.

Kinetic Study

Reaction Order

The kinetic parameters of the interaction of arenesulfinic acids with 2-bromo-1,3-diphenyl-2-propenone and 3-bromo-4-phenyl-3-butene-2-on were determined. The interactions are second order reactions, but they are first order regarding each reagent. The overall reaction order was determined by using the Van't Hoff method and the half-time method in the concentration interval 0.15–10 M. The overall reaction order for the nucleophilic addition of benzensulfinic acids to 2-bromo-1,3-diphenyl-2-propenone was calculated to be 1.71 (Table II),

TABLE II Experimental Proof of the Benzensulfinic Acids Addition Order to 2-Bromo 1,3-Diphenyl-2-Propenone by the Methods of Van't Hoff and Half-Time in the Concentration Range 0.01–10 M, T = 298 K

Concentration Range C, M	0.01–0.1	0.1–1	1–5	5–10
Order value by the Van't Hoff Method	1.67	1.65	1.69	1.67
Order Value by the half-time method	1.74	1.76	1.77	1.75

TABLE III Experimental Proof to the Benzenesulfinic Acids Addition Order to 3-bromo-4-Phenyl-3-Butene-2-On by the Methods of Van't Hoff and Half-Time in the Concentration Range 0.01–10 M, T = 298 K

Concentration Range C, M	0.01–0.1	0.1–1	1–5	5–10
Order value by the Van't Hoff Method	1.60	1.59	1.62	1.58
Order Value by the half-time method	1.70	1.75	1.78	1.77

and the reaction order for the interaction between 3-bromo-4-phenyl-3-butene-2-on and benzenesulfinic acid was found to be 1.67 (Table III). These calculations can also be proved by the linear dependence 1/[bromochalkone] = f(τ). Slopes of straight lines for these dependences were used to calculate rate constants for five different temperatures. The activation energy and the enthalpy of activation were determined using the Arrhenius equation (Table IV).

Effect of the Substituents

Rate constants for the addition of arenesulfinic acids to bromochalkones are presented in Table IV. These results and the

TABLE IV Substituent Effect on Rate Constants and Addition Parameters at Different Temperatures

Nusleophile	Subst. Rate	Temp. K	K · 10^4 $m^{-1}.s^{-1}$	E kJ · mol^{-1}	ΔH ≠ kJ · mol^{-1}
1	**2b**	288	1.17 ± 0.3	49.01	48.76
		293	1.93 ± 0.5		
		298	2.73 ± 0.4		
		303	4.29 ± 0.6		
		308	7.10 ± 0.3		
1	**2c**	288	6.67 ± 0.2	52.81	52.56
		293	0.87 ± 0.6		
		298	0.96 ± 0.4		
		303	1.23 ± 0.5		
		308	1.50 ± 0.3		
4	**2b**	288	2.06 ± 0.8	46.09	45.85
		293	3.65 ± 0.6		
		298	5.28 ± 0.7		
		303	9.14 ± 0.9		
		308	14.58 ± 1.1		
4	**2c**	288	1.00 ± 0.2	50.66	50.42
		293	1.13 ± 0.4		
		298	1.41 ± 0.3		
		303	1.62 ± 0.2		
		308	2.06 ± 0.6		

calculated Hammet's constants show that the methyl group in the p-position in the benzene ring of the sulfinic acid accelerates the reaction, while the chlorine atom in the same position has the opposite effect.

The addition of a bromine atom to an ά-carbon atom of the carbon–carbon double bond decreases the activity of the bond regarding nucleophilic reagents. A comparison of rate constants shows that nitrochlkones are more active toward these reagents in the nucleophilic reactions than bromochakones.

EXPERIMENTAL

Methods

Melting points were determined on a Melt-Temp apparatus and are uncorrected. Microanalyses were obtained using an elemental Analyzer-1104 (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 with a Bruker 350 MHz spectrometer, using $CDCl_3$ solution.

The Typical Procedure for the Preparation of 3-Arylsulfonyl-2-bromo-1,3-diphenylpropanones 3 and 4-arylsulfonyl-3-bromo-4-phenyl-2-butanones (5)

To 1,3-diphenyl-2-bromopropenone (3-bromo-4-phenyl-3-butene-2-on) (0.01 mol) in 95% ethanol was added sulfinic acid (0.01 mol). The reaction mixture was kept standing at 20°C for 10 h to yield the substituted ketosulfones. The crystals obtained were filtered and recrystallized from toluene.

Selected Data for 3a

IR (ν, cm^{-1}, KBr): 1663 (CO—Ph); 1297 ($\nu^{as}_{SO_2}$); 1135 ($\nu^{s}_{SO_2}$). UV (λ max., nm (EtOH); lg ε): 206 (2.85); 258 (3.06); 313 (3.10). ^{1}H NMR (δ) $CDCl_3$: 7.20–7.80 (m, 15 H); 5.12 (d, CH); 6.11 (d, CH).

Selected Data for 3b

IR (ν, cm^{-1}, KBr): 1667 (CO—Ph); 1300 ($\nu^{as}_{SO_2}$); 1135 ($\nu^{s}_{SO_2}$); UV (λ max., nm (EtOH); lg ε): 207 (3.01); 258 (2.99); 317 (3.21). ^{1}H NMR (δ) $CDCl_3$: 7.23–7.82 (m, 14 H); 5.10 (d, CH); 6.13 (d, CH); 2, 40 (s, CH_3).

Selected Data for 3c

IR (ν, cm^{-1}, KBr): 1667 (CO—Ph); 1313 ($\nu^{as}_{SO_2}$); 1140 ($\nu^{s}_{SO_2}$). UV (λ max., nm (EtOH); lg ε): 206 (2.94); 260 (3.09); 318 (3.19). ^{1}H NMR (δ, CDCl$_3$: 7.18–7.78 (m, 14 H); 5.13 (d, CH); 6.12 (d, CH).

Selected Data for 5a

IR (ν, cm^{-1}, KBr): 1702 (CO); 1295 ($\nu^{as}_{SO_2}$); 1140 ($\nu^{s}_{SO_2}$). UV (λ max., nm (EtOH); lg ε): 224 (2.19); 254 (3.00); 297 (3.03). ^{1}H NMR (δ, CDCl$_3$, 7.24–7.82 (m, 10 H); 5.13 (d, CH); 6.11 (d, CH).

Selected Data for 5b

IR (ν, cm^{-1}, KBr): 1705 (CO); 1295 ($\nu^{as}_{SO_2}$); 1140 ($\nu^{s}_{SO_2}$). UV (λ max., nm (EtOH); lg ε): 225 (3.27); 252 (3.11); 296 (3.24). ^{1}H NMR (δ, CDCl$_3$: 7.20–7.75 (m, 9 H); 5.10 (d, CH); 6.14 (d, CH); 2.41 (s, CH$_3$).

Selected Data for 5c

IR (ν, cm^{-1}, KBr): 1750 (CO); 1305 ($\nu^{as}_{SO_2}$) 1140 ($\nu^{s}_{SO_2}$). UV (λ max., nm (EtOH); lg ε): 225 (3.33); 253 (3.21); 296 (3.39). ^{1}H-NMR (δ, CDCl$_3$: 7.23–7.81 (m, 9H); 5.12 (d, CH); 6.13 (d, CH).

Rate Measurement

Purified benzenesulfinic acids (0.001 mol) were added to the corresponding bromoketones (0.001 mol) in ethanol (50 mL). Aliquots were taken out at regular intervals of time and diluted with ethanol. Flow concentrations of reagents during the reaction were determined by means of UV spectrophotometry. The second-order constants, activation energy, and enthalpy of activation were calculated according to the literature.

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