

STUDIES ON THE STRUCTURE OF HALOGENATED DERIVATIVES OF SOME KETOSULFONES

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ABSTRACT

The compounds studied have been synthesized by nucleophilic addition of arenesulfinic acids to bromochalcones. Sophisticated instrumental methods such as FT – IR, UV and NMR were employed to study the chemical structure of the corresponding bromine-containing derivatives and both the X-ray analysis and semi-empirical methods were used to examine their molecular geometry.

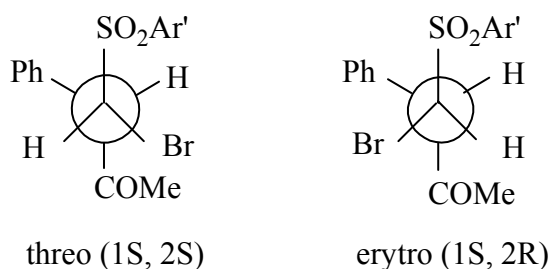
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INTRODUCTION

The respect work is a continuation of our previous studies on the methods of preparation of chalcones as well as the evaluation their reactivity and possible fields of application [1,2]. Two major groups of nitro- and bromochalcones were synthesized in the course of our work, and their structure and reactivity towards sulfur-containing nucleophiles were also studied. As a result, two principal groups of polyfunctional sulfones were synthesized. The objective of the present work was to investigate the structure of this type organic compounds, since such studies are closely associated with some fundamental issues in organic chemistry such as structure – reactivity relationships, electronic effects, region – and stereoselectivity of organic reaction etc. The studies on the fine structure of these compounds are considered to be of significant importance, since this could give rise to the adoption of some new synthetic approaches and the use of ketosulfones as products of potential biological activity, e.g. their possible utilization as anti – malarial, anti-inflammatory and antibiotic drugs.

DISCUSSION

The methods for preparation of the corresponding compounds are described. The molecules contained two chiral centers, determining the specific stereochemistry.



- (1) - o-MeC₆H₄; (2) -p-MeC₆H₄; (3)- p-BrC₆H₄;
 (4) - p-IC₆H₄; (5)- 1,2-C₁₀H₇; (6) - p-NO₂C₆H₄;
 (7)- p-AcNHC₆H₄; yield 60 -75%

The attempts to separate and isolate the two stereoisomers were unsuccessful. For this reason, the studies of a diastereomer mixture (70 : 30 with predominance of threo-form) were conducted. The spectral studies definitely confirmed the structures of the compounds studied. Strong absorption bands, corresponding to both the asymmetric and symmetric stretching vibrations of sulfonyl group were observed in the 1313 – 1300 and 1140 – 1130 cm⁻¹ regions respectively. The absorption band for the carbonyl group was registered at 1705 – 1695 cm⁻¹. Skeleton vibrations of benzene rings were characterized by the bands at 1640 – 1450 cm⁻¹, and out - of-plane C – H aryl vibrations within 725 – 720 and 830 – 790 cm⁻¹ proved the presence of mono-substituted and p-substituted benzene rings, respectively.

The stretching vibrations, corresponding to C – Br bond were observed at 680 - 660 cm⁻¹. The presence of halogen atom did not influence the location of the characteristic bands for the ketogroup. The typical absorption maximum for the carbonyl group in the UV spectra of the corresponding studied was observed at 300 – 310 nm (lg ε = 3.10 – 3.42). In this case, no electronic effects involving the sulfonyl group could be assumed. Aromatic multiplet signals within 7.00 – 7.80 ppm were registered in the corresponding NMR spectra. Two doublets at 5.15 and 6.22 ppm were also observed. The data from the corresponding integral curves indicated that each doublet corresponded to one proton. NMR data also showed that the ketosulfones as reaction products represented a mixture of two stereoisomers. The X-ray diffraction studies confirmed that ketosulfones were representatives of the triclinic crystallographic system. Several possible crystal lattices were assumed, from which, the one suggested in this work was found to have the smallest volume and corresponded best to the experimental data. Following the determination of the symmetry, the type, the volume of the elementary cell and the exact density of the crystal, the number of the structural units was found. The molecular volumes as well as other specific dimensions were also determined. The most probable locations of the molecule as symmetric motif of the elementary cell were selected. Following further transformation of the Decart coordinates into partial ones, the geometry of the intensive distribution was calculated and was compared to the one found experimentally.

Table 1. Characterization data of the synthesized compounds

Comp No	m.p. °C	Formula mol.wt	Analysis (%) calc (found)			IR(ν , cm^{-1}) KBr	UV/VIS λ_{max} , nm (lg ϵ)	$^1\text{H NMR}$ (CDCl_3 ,
			C	H	S			
1	154	$\text{C}_{17}\text{H}_{17}\text{BrO}_3\text{S}$ (381)	53.54 (52.10)	4.45 (3.80)	8.40 (8.72)	1725 (CO), 1300-1130 (SO_2), 660 (C - Br)	220 (2.80); 252 (3.20); 305 (3.25)	7.20-7.80 (m, 9H) 5.15 (d,CH), 6.20 (d, CH), 2.42 (s, CH_3)
2	161	$\text{C}_{17}\text{H}_{17}\text{BrO}_4\text{S}$ (397)	51.39 (50.25)	4.29 (3.75)	8.05 (8.15)	1720 (CO), 1305-1130 (SO_2), 660 (C - Br)	215 (2.72); 252 (3.10); 310 (3.20)	7.20-7.82 (m, 9H) 5.16 (d,CH), 6.22 (d, CH), 2.42 (s, CH_3)
3	168	$\text{C}_{16}\text{H}_{14}\text{Br}_2\text{O}_3\text{S}$ (446)	43.05 (42.70)	3.14 (2.85)	7.17 (6.68)	1725 (CO), 1300-1135 (SO_2), 680 (C - Br)	218 (2.75); 252 (3.20); 300 (3.20)	7.15-7.75 (m, 9H) 5.17 (d,CH), 6.20 (d, CH), 2.40 (s, CH_3)
4	182	$\text{C}_{16}\text{H}_{14}\text{BrIO}_3\text{S}$ (493)	38.94 (38.30)	2.84 (3.10)	6.49 (6.12)	1720 (CO), 1310-1130 (SO_2), 680 (C - Br)	216 (2.72); 252 (3.18); 305 (3.22)	7.10-7.70 (m, 9H) 5.20 (d,CH), 6.20 (d, CH), 2.40(s, CH_3)
5	193	$\text{C}_{20}\text{H}_{17}\text{BrO}_3\text{S}$ (417)	57.55 (57.10)	4.08 (3.60)	7.67 (7.20)	1725 (CO), 1312-1132 (SO_2), 680 (C - Br)	218 (2.72); 252 (3.20); 302 (3.20)	7.15-7.78 (m, 9H) 5.18 (d,CH), 6.22 (d, CH), 2.40 (s, CH_3)
6	189	$\text{C}_{16}\text{H}_{14}\text{BrNO}_5\text{S}$ (412)	46.67 (45.90)	3.40 (3.10)	7.76 (8.10)	1723 (CO), 1313-1135 (SO_2), 675 (C - Br)	212 (2.70); 254 (3.22); 305 (3.18)	7.20-7.80 (m, 9H) 5.15 (d,CH), 6.20 (d, CH), 2.42 (s, CH_3)
7	197	$\text{C}_{18}\text{H}_{18}\text{BrNO}_4\text{S}$ (424)	50.94 (51.20)	4.25 (3.90)	7.55 (7.10)	1720 (CO), 1310-1140 (SO_2), 680 (C - Br)	216 (2.72); 254 (3.22); 310 (3.24)	7.20-7.80 (m, 9H) 5.20 (d,CH), 6.20 (d, CH), 2.42 (s, CH_3)

EXPERIMENTAL

Bromochalcones were prepared and purified as described in the literature.

IR and UV spectra were obtained using Bruker and Specord UV-VIS. NMR (chemical shifts measured in deuterated solvents are given in ppm from TMS) spectra were recorded with a Bruker 350 MHz spectrometer, using CDCl₃ solution. X-ray studies were made on a URD-6 diffractometer using a β -filtered for the C_{uk α} emission, at scanning rate 1°2 θ /min in the interval 3 - 60 °2 θ . The integral intensities were determined planimetrically.

Microanalyses were obtained using an elemental Analyzer – 1104 (Carlo Erba).

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