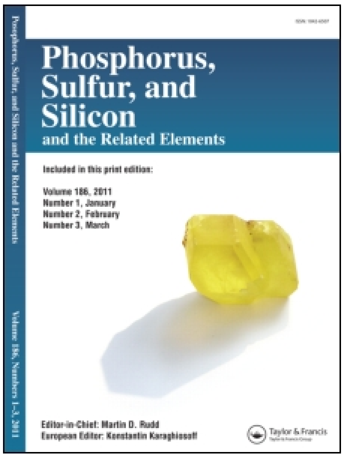

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CYCLIZATION OF SELECTED BENZYL SULFONE DERIVATIVES UNDER PHASE TRANSFER CATALYTIC CONDITIONS

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CYCLIZATION OF SELECTED BENZYL SULFONE DERIVATIVES UNDER PHASE TRANSFER CATALYTIC CONDITIONS

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Abstract Seven selected benzyl chloroalkyl sulfones (la-c) and benzyl carboethoxyalkyl sulfones (ld-g) has been subjected to treatment with aqueous NaOH(50%) under PTC conditions. Analysis of the product mixtures revealed competitive cyclization, elimination and hydrolysis reactions. Correlation of the reaction products and the starting sulfone has been discussed.

INTRODUCTION

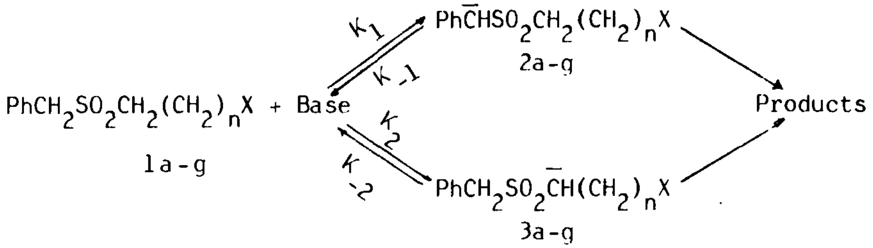
The capacity of sulfur in its various oxidation states to enhance significantly the acidity of adjacent C-H bonds has been reported as early as 1889 by Fromm[1]. While precise mechanism of stabilization of carbanions by adjacent sulfur, in its various oxidation conditions, is still controversy, the great importance of this effect in synthetic organic chemistry is controvertible[2]. For example, cyclization of aryl 3-halogenopropyl sulfones under strongly basic conditions was studied by several authors[3,4]. Competition between cyclization, external substitution and elimination reactions has been reported when aryl ω-halogenoalkyl sulfones react with alkoxides[5]. Also, cyclopropanation of methylene group activated with sulfone group[6,7] and other valuable synthetic reactions were described[8-16]. These results suggested the formation of α-sulfonylcarbanion intermediates. From these studies, in addition to our interest in sulfur chemistry[17,18], we present in this work the treatment of some benzyl sulfone derivatives with aqueous sodium hydroxide solution under PTC conditions. The selected sulfones were carefully designed to have two active centers each capable to form anion (ambident carbanion) under the working conditions.

RESULTS AND DISCUSSION

This work aims to study the cyclization of benzyl sulfone derivatives under PTC condition and the competing reactions. The title sulfones include: benzyl 2-chloroethyl sulfone (1a), benzyl 3-chloropropyl sulfone (1b), benzyl 4-chlorobutyl sulfone (1c), ethyl 2-benzylsulfonylacetate (1d), ethyl 3-benzylsulfonylpropionate (1e), ethyl 4-benzylsulfonylbutyrate (1f), and ethyl 5-benzylsulfonylvalerate (1g).

As indicated in Table 1 (entry 1), treatment of 1a under PTC conditions gave a mixture of benzyl vinyl sulfone (4), benzyl 2-hydroxyethyl sulfone (6) and 2-phenylthiaetane-S,S-dioxide (5). In case of 1b (Table 1, entry 2), benzyl 1-propenyl sulfone (7), benzyl 2-propenyl sulfone (8), 2-phenyl-2,3,4,5-tetrahydrothiophene-S,S-dioxide (9) in addition to benzyl cyclopropyl sulfone (10) were formed. Similarly, 1c gave a mixture of benzyl 3-butenyl sulfone (11), benzyl 2-butenyl sulfone (12), 2-phenylthiane-S,S-dioxide (13) and benzyl cyclobutyl sulfone (14).

Formation of 5,9 and 13 could be explained through intramolecular substitution reaction of the carbanions 2a,b,c while formation of 10 and 14 is expected from 3b,c, respectively. The main competing reaction, viz. elimination reaction has resulted on the formation of 4 from 1a, 7 and 8 from 1b, and 11 and 12 from 1c. This is easily explained as a result of dehydrohalogenation reaction. Formation of 6 could be visualized as a nucleophilic displacement of the Cl^- by $\bar{O}H$.



Compd.	n	X		Compd.	n	X
1a	1	Cl	;	1e	1	$CO_2C_2H_5$
1b	2	Cl	;	1f	2	$CO_2C_2H_5$
1c	3	Cl	;	1g	3	$CO_2C_2H_5$
1d	0	$CO_2C_2H_5$				

In an endeavour to obtain cyclic ketosulfones, 1d-g were prepared and subjected to treatment with NaOH solution as mentioned before. While the corresponding cyclic ketosulfones 15,17,19 and 21 were formed in low to fairly moderate yield (8-25%), the major reaction product is the parent acid. Attempts to improve the yield of the cyclization products are in progress.

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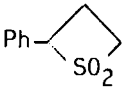
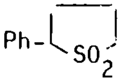
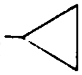
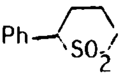
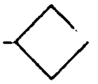
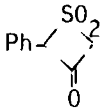
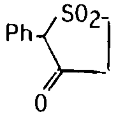
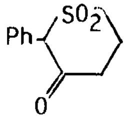
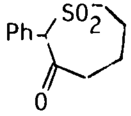
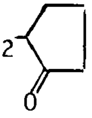
TABLE I Treatment of la-q with NaOH soln. under PTC conditions.

Entry	Starting Sulfone	Products (No., % yield)^{1,2}
1	la	$PhCH_2SO_2CH{=}CH_2$ (4, 38),  (5, 12), $PhCH_2SO_2CH_2CH_2OH$ (6,8).
2	lb	$PhCH_2SO_2CH_2CH{=}CH_2$ (7, 22), $PhCH_2SO_2CH{=}CHCH_3$ (8,25),  (9, 20), $PhCH_2SO_2$ (10, 11).
3	lc	$PhCH_2SO_2CH_2CH_2CH{=}CH_2$ (11,30), $PhCH_2SO_2CH_2CH{=}CHCH_3$ (12,33),  (13,12), $PhCH_2SO_2$ (14,8).
4	ld	 (15,15), $PhCH_2SO_2CH_2CO_2H$ (16,65).
5	le	 (17,20), $PhCH_2SO_2CH_2CH_2COOH$ (18,50).
6	lf	 (19,25), $PhCH_2SO_2(CH_2)_3COOH$ (20,50).
7	lg	 (21,8), $PhCH_2SO_2$ (22, 10) $PhCH_2SO_2(CH_2)_4COOH$ (23, 59).

1 All experiments were carried out at 100°C for 12 hrs using $(n\text{-}C_4H_9)_4N^+Br^-$ catalyst, aqueous NaOH solution (50%) base and benzene solvent.

2 Other minor degradation products such as $PhCH_2SH$ and $PhCH_2SO_2H$ were also detected.