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DEHYDROCHLORINATION OF α -CHLORO SULFONES WITH KOH-T-BUOH: KINETIC VS EQUILIBRIUM CONTROL OF THE FORMATION OF α , β -UNSATURATED SULFONES AND THE β -T-BUTOXY AND β -HYDROXY MICHAEL ADDUCTS

Vera M. Kolb^a; Duy H. Hua^a; Cal Y. Meyers^a

^a Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, USA

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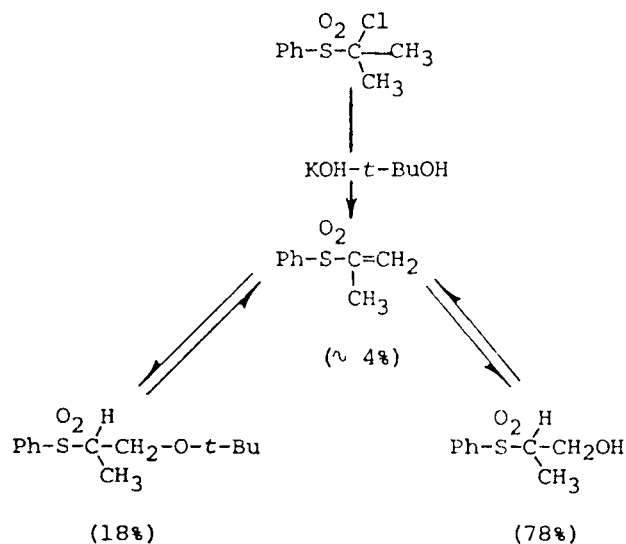
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DEHYDROCHLORINATION OF α -CHLORO SULFONES WITH KOH-t-BuOH:
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MICHAEL ADDUCTS

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
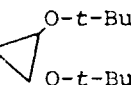
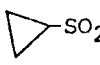


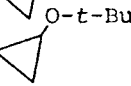
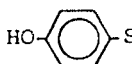
Department of Chemistry and Biochemistry, Southern Illinois
University, Carbondale, Illinois 62901, USA

Dehydrochlorination of a series of aryl α -chloroalkyl sulfones with powdered KOH in t-BuOH was investigated (Table). The initial product of these reactions, an α,β -unsaturated sulfone, is generally detected in only small amounts since β -hydroxy and β -t-butoxy derivatives are formed from relatively rapid Michael addition of HO^- and t-BuO $^-$. These addition reactions are reversible and reflect kinetic and equilibrium control: While t-BuO $^-$ apparently adds faster than HO^- , the hydroxy adduct generally is thermodynamically favored. In those cases where specific substitution reduces the stability of the α -sulfonyl carbanions, the rates of the Michael additions and equilibrations are likewise reduced and the α,β -unsaturated sulfones can be isolated as the major products. An example of the equilibria is shown:



Most of these α -chloro sulfones were prepared by the reaction of the parent sulfone with CCl_4 -KOH-*t*-BuOH at 25° . Only at higher temperatures does dehydrochlorination become noticeable. Thus, when the dehydrochlorinations are carried out in the presence of CCl_4 at 60 - 80° the Michael adducts that are formed are themselves rapidly α -chlorinated. Significantly, the β -*t*-butoxy- α -chloro sulfones thus formed are resistant to dehydrochlorination under these conditions. Some of these reactions and products are compared in the Table.

Reactions of Aryl α -Chloroalkyl Sulfones with KOH-*t*-BuOK at 60 - 80°

Substrate ¹	Product Isolated	Yield %
$\text{PhSO}_2\text{CCl}_3$	PhSO_3H	100
Ph-SO_2 	Ph-SO_2 	86
 	 	~ 90
$\text{PhSO}_2\text{CCl}(\text{CH}_3)_2$	$\left[\begin{array}{l} \text{PhSO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH} \\ \text{PhSO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O-}t\text{-Bu} \\ \text{PhSO}_2\text{C}(\text{CH}_3)=\text{CH}_2 \end{array} \right]$	 78 18 ~ 4
$\text{PhSO}_2\text{CCl}(\text{CH}_3)_2 + \text{CCl}_4$	$\text{PhSO}_2\text{CCl}(\text{CH}_2\text{O-}t\text{-Bu})_2$	20
$\text{ArSO}_2\text{CCl}_2\text{CH}_3 + \text{CCl}_4$ (Ph or Mes)	$\text{ArSO}_2\text{CCl}_2\text{CH}_2\text{O-}t\text{-Bu}$	95
 $\text{SO}_2\text{CCl}(\text{CH}_3)_2$	$\left[\begin{array}{l} \text{HO-} \langle \text{benzene ring} \rangle \text{SO}_2\text{C}(\text{CH}_3)=\text{CH}_2 \\ \text{HO-} \langle \text{benzene ring} \rangle \text{SO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH} \\ \text{HO-} \langle \text{benzene ring} \rangle \text{SO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O-}t\text{-Bu} \end{array} \right]$	 ~ 30 ~ 15 ~ 15
		~ 60

¹With the exception of the last entry, these substrates were prepared by the reaction of the parent sulfone with CCl_4 -KOH-*t*-BuOH at 25° . The α -bromo systems generally provided similar results but at greater rates.