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

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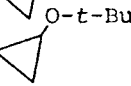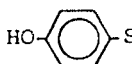
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Dehydrochlorination of a series of aryl α-chloroalkyl sulfones
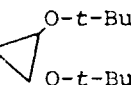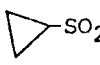with powdered KOH in t-BuOH was investigated (Table). The ini-
tial product of these reactions, an α,β-unsaturated sulfone, is
generally detected in only small amounts since β-hydroxy and β-
t-butoxy derivatives are formed from relatively rapid Michael
addition of HO⁻ and t-BuO⁻. These addition reactions are rever-
sible 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 sub-
stitution reduces the stability of the α-sulfonyl carbanions,
the rates of the Michael additions and equilibrations are like-
wise reduced and the α,β-unsaturated sulfones can be isolated
as the major products. An example of the equilibria is shown:
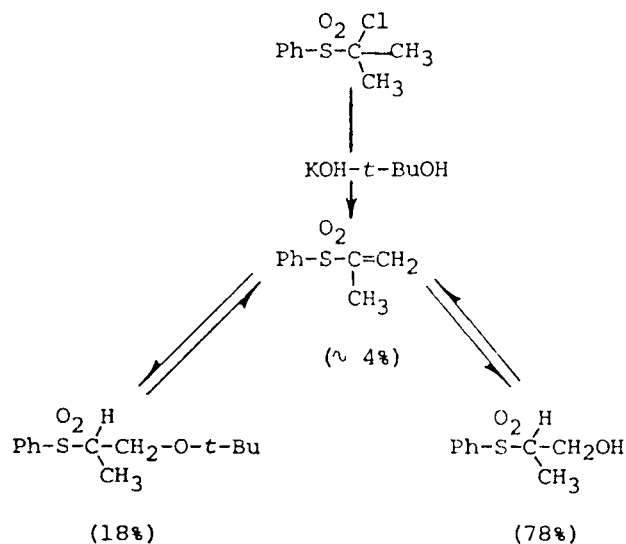
Most of these α-chloro sulfones were prepared by the reaction
of the parent sulfone with CCl_4-KOH-t-BuOH at 25°. Only at
higher temperatures does dehydrochlorination become noticeable.
Thus, when the dehydrochlorinations are carried out in the pres
ence of CCl_4 at 60-80° the Michael adducts that are formed are
themselves rapidly α-chlorinated. Significantly, the β-t-
butoxy-α-chloro sulfones thus formed are resistant to dehydro-
chlorination 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 %
$PhSO_2CCl_3$	$PhSO_3H$	100
Ph-SO$_2$–(cyclopropyl with Cl, Cl)	Ph-SO$_2$–(cyclopropyl with O-t-Bu, O-t-Bu)	86
(cyclopropyl)–SO$_2$–(cyclopropyl with Cl, Cl)	(cyclopropyl)–SO$_2$–(cyclopropyl)	∿ 90
$PhSO_2CCl(CH_3)_2$	$PhSO_2CH(CH_3)CH_2OH$	78
	$PhSO_2CH(CH_3)CH_2O$-t-Bu	18
	$PhSO_2C(CH_3)=CH_2$	∿ 4
$PhSO_2CCl(CH_3)_2 + CCl_4$	$PhSO_2CCl(CH_2O$-t-Bu$)_2$	20
$ArSO_2CCl_2CH_3 + CCl_4$ (Ph or Mes)	$ArSO_2CCl_2CH_2O$-t-Bu	95
HO–(C$_6$H$_4$)–$SO_2CCl(CH_3)_2$	HO–(C$_6$H$_4$)–$SO_2\overset{CH_3}{\underset{}{C}}=CH_2$ ∿ 30	∿ 60
	HO–(C$_6$H$_4$)–$SO_2CH(CH_3)CH_2OH$ ∿ 15	
	HO–(C$_6$H$_4$)–$SO_2CH(CH_3)CH_2O$-t-Bu ∿15	

[1]With 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 pro-
vided similar results but at greater rates.

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