Synthese en reactiviteit van enige α-halosulfonen

Middelbos, Willem

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SUMMARY

This thesis deals with the synthesis of a variety of substituted \(\alpha\)-chlorosulfones by reaction of \(\alpha\)-diazosulfo-
nes with electrophilic reagents and in addition, the reaction of some \(\alpha\)-halosulfones with nucleophiles and bases.

After an introductory chapter the reaction of \(\alpha\)-diazo-
sulfones with tert. butyl hypochlorite \(t.BuOC\) sulfuryl chloride and sulfenyl halides is described in the chapters 2, 3 and 4, respectively. The results of these reactions are summarized in Scheme 1.

In each chapter the mechanism of the observed reac-
tions is discussed. For the reaction of \(\alpha\)-diazosulfones with tert. butyl hypochlorite in dichloromethane it is assumed that the initially formed diazonium-ion collapses with the counterion \(t.BuO^-\) with concomitant liberation of nitrogen. Similarly the product from \(\alpha\)-diazo-
sulfones and sulfenyl halides can be explained. For the reaction with \(t.BuOC\) in tert. butyl alcohol, ethyl alcohol or methyl alcohol an alcoholyzes of the intermediate diazoniumion is proposed. In the reaction of \(\alpha\)-diazosulfones with sulfu-
ryl chloride in ethers, such as diethyl ether, ethylene
oxide, oxetane, tetrahydrofuran and tetrahydropyran, the diazonium ion is solvolyzed by an ether molecule which results in an ether cleavage reaction. With acetals and orthoesters as solvents a similar process takes place.

For comparison some reactions were carried out with \( \alpha \)-diazoketones and ethyl diazoacetate (see Scheme 2).

\[
\text{SCHEME - 2}
\]

\[
\begin{align*}
\text{RCOCH}_2\text{N}_2 & \xrightarrow{\text{tBuOCl}/\text{CH}_2\text{Cl}_2} \text{RCOCH}_2(\text{Cl})\text{O-tBu} \\
\text{RCOCH}_2\text{N}_2 & \xrightarrow{\text{tBuOCl}/\text{ROH}} \text{RCOCH}_2(\text{OR})_2 \cdot \text{HCl} \\
\text{SO}_2\text{Cl}_2/\text{R}^\prime \text{OR}^\prime & \xrightarrow{\text{VIII}} \text{RCOCH}_2(\text{Cl})\text{O-tBu} / \text{RCl}
\end{align*}
\]

The reactions of those diazo compounds with \( t \).BuOCl in dichloromethane or \( \text{SO}_2\text{Cl}_2 \) in ethers takes a course analogous to those depicted in Scheme 1. In alcoholic solution however \( \alpha \)-diazoketones did not give the \( \alpha \)-alkoxy \( \alpha \)-chlorocarbonyl compounds, but dialkyl acetals were isolated since \( \alpha \)-alkoxy-\( \alpha \)-chlorocarbonyl compounds react readily with alcohols to give acetals.

In chapter 4 the Ramberg Bäcklund rearrangement of compounds of the types \( \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH(Cl)XR} \ (X = \text{O,S}) \), \( \text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{C(CH}_3)_2 \text{ClSR} \) and \( \text{C}_6\text{H}_5\text{CH(CH}_3)_2\text{SO}_2\text{CH(Cl)SR} \) with some bases is described. The ultimate products of the rearrangement are alkenyl ethers and thioethers. It was found that the reaction showed a high degree of stereospecificity, the \( E/Z \) ratio of the alkenes obtained depends on the nature of the base. The rearrangement is assumed to proceed via an episulfone as an intermediate which then looses \( \text{SO}_2 \) by stereospecific \( cis \)-elimination to give an alkene. The stereospecific formation of the episulfone is a process involving a selective abstraction of an \( \alpha \)-proton from a preferred conformation of the substrate,
a subsequent inversion at $C_2$ and then an internal SN$_2$-reaction with the expulsion of the chloride anion. This double inversion mechanism explains the preferential formation of the Z-episulfone. The so formed Z-episulfone however, can epimerize under influence of base to the E-episulfone. (See Scheme 3).

**SCHEME - 3**

Replacing of an $\alpha$- or an $\alpha'$-H-atom by a methylgroup shows a decrease of the stereospecificity of the Ramberg Bäcklund rearrangement.

In chapter 6 the reaction of bromomethyl and chloromethyl and dichloromethyl p.tolyl sulfone with sodium thiolates is described. There is a striking difference between the reaction of aliphatic sodium thiolates with chloromethyl p.tolyl sulfone and bromomethyl p.tolylsulfone. In the first case a substitution of the chlorine by a SR-group is observed, while in the latter only a reduction to methyl p. tolyl sulfone takes place. With aromatic sodium thiolates chloromethyl and bromomethyl p. tolyl sulfone both gave a substitution of the halogenatom by an ArS-group.

The reaction of dichloromethyl p-tolyl sulfone with aliphatic sodium thiolates gave a reduction to chloromethyl p. tolyl sulfone. However with sodium thiophenolate to a more complex reactionmixture was obtained.
It is assumed that the displacement of the halogen atom by hydrogen or a SR-group proceeds via an initial attack of $RS^-$ on halogen to yield an $\alpha$-sulfonylcarbanion which then either is protonated by the solvent (ethanol) or reacts with the intermediate sulfenyl halide (See Scheme 4)

**SCHEME 4**

\[
\begin{align*}
RSO_2CH_2X + RS^- &\rightarrow RSO_2CH^- + R'SX \\
\text{or} &\rightarrow RSO_2CH_2SR' + X^-
\end{align*}
\]

In appendix A a simple method is described for the reaction of dihalomethyl sulfones from the reaction of dihalocarbene (from haloform and aqueous base) with sulfinate anion.

\[
\begin{align*}
RSO_2Na + CHX_3 &\xrightarrow{\text{KOH}} RSO_2CHX_2^+ + Na^+ + H_2O
\end{align*}
\]

Appendix B deals with some efforts to synthesize $\alpha$-halo-$\alpha$-diazosulfones from the reaction of the corresponding mercury-bis ($\alpha$-diazosulfones) and halogens. No $\alpha$-halo-$\alpha$-diazosulfone could be obtained which is in contrast to the preparation of ethyl halodiacetates from mercury-bis (ethyl diazoacetate) and halogens. Ethyl iododiazooacetate was prepared by direct halogenation of ethyl diazoacetate with iodine in the presence of triethylamine. This new method however failed for the synthesis of $\alpha$-halo-$\alpha$-diazosulfones.