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Synthesis and Reactivity of Allylic and Propargylic Trichloromethanesulfinates

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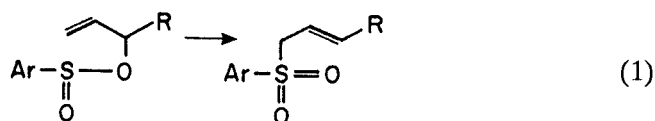
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SYNTHESIS AND REACTIVITY OF ALLYLIC AND PROPARGYLIC TRICHLOROMETHANESULFINATES

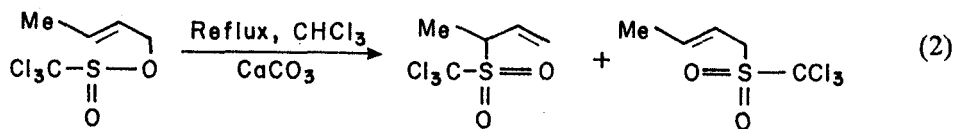
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Abstract The synthesis and rearrangement of the title compounds to sulfones are discussed. A facile isomerization of the allylic trichloromethyl sulfones to the corresponding vinyl sulfones is also described.

The rearrangement of allylic and propargylic arenesulfinates to allylic and allenic aryl sulfones, respectively, have been discovered by us over two decades ago and have been suggested to occur by a concerted [2,3]-sigmatropic mechanism.¹ More recently, we have shown that benzyl trichloromethanesulfinates (trichlinates) exhibit unusual high reactivity and undergo rearrangement and solvolysis with remarkable rate enhancements, due to the excellent leaving group ability of the trichlinate group, comparable to the tosylate group.² Prompted by these results, which have been explained by an ionization mechanism, we have decided to investigate the effect of substitution of the aryl by the trichloromethyl group on the concertedness of the [2,3]-sigmatropic rearrangement of allylic and propargylic sulfinates to sulfones.



The synthesis of allyl and propargyl trichlinates and several of their α - or γ -substituted derivatives was accomplished by a modification of a novel general procedure recently reported by Sharpless.³ This method is based on the reaction of alcohols with sulfinyl chlorides generated *in situ* by reduction of the corresponding sulfonyl chloride with $(\text{MeO})_3\text{P}$. A comparison of the reactivity of allylic trichlinates and arenesulfinates has indicated the following differences. First, unlike the rearrangement of unsymmetrically substituted allylic arenesulfinates which proceeds with full simultaneous 1,3-allylic shift, the rearrangement of the corresponding trichlinates affords a mixture of both isomeric sulfones (Eq. 2). Second, in contrast to allylic arenesulfinates which rearrange exclusively to sulfone even under solvolytic conditions, the rearrangement of the corresponding



trichlinates may be accompanied by solvolysis products in certain cases such as the cinnamyl ester. Third, while the rearrangement of allylic arenesulfonates exhibits a small sensitivity to the substituent effect, the rearrangement of allylic trichlinates exhibits a pronounced effect. Thus, the rearrangement of cinnamyl trichlinate is 10^4 faster than the allyl ester. Finally, the reactivity of allylic trichlinates in general is faster. However, while cinnamyl trichlinate rearranges by 10^3 faster than cinnamyl arenesulfonate, allyl trichlinate rearranges faster by a factor of 3 only. These results confirm the hypothesis that by changing the leaving group from arenesulfonate to trichlinate, the mechanism may change from a concerted [2,3]-sigmatropic mechanism to an ionic one, especially when the intermediate carbonium ion is highly stabilized.

Preliminary results indicate that unlike allylic trichlinates, propargylic trichlinates undergo full [2,3]-sigmatropic rearrangement. Thus, α -methyl, α,α -dimethyl, and α -methyl- α -phenylpropargyl trichlinates rearranged to γ -methyl, γ,γ -dimethyl and γ -methyl- γ -phenylallenyl trichlones, respectively. The last rearrangement occurs even at low temperature. Furthermore, the rearrangement of optically active α -methylpropargyl trichlinate affords optically active γ -methylallenyl trichlone, when conducted in toluene.

Finally, we have found an interesting isomerization of allylic trichlones to vinylic trichlones which proceeds very easily even in the presence of weak bases such as 2,6-lutidine and triethylamine. Such an easy isomerization was not detected with any of the aryl sulfones examined. This reaction is not only of mechanistic interest, but also of synthetic utility due to the growing importance of vinyl sulfones in organic synthesis in recent years.⁴

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