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NEW ACTIVE SULFUR TRANSFER REAGENTS: ARENETHIOSULFENYL CHLORIDES. A CONVENIENT SYNTHESIS OF EPISULFIDES FROM OLEFINS

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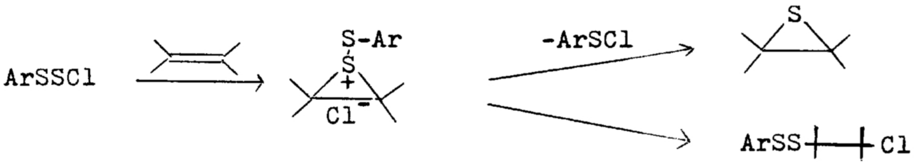
Arenethiosulfenyl chlorides, readily prepared from the corresponding thiophenols and sulfur dichloride, reacted with olefins to give disulfide adducts, which could easily be transformed into episulfides in good yields by treatment with sodium amide or sulfide. The episulfidation of olefins has been shown to be stereospecific, since trans- and cis-2-butenes afforded the corresponding trans and cis episulfides, respectively.

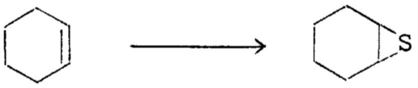
We wish to report a new series of sulfur transfer reagents to olefins, arenethiosulfenyl chlorides, which are effective for episulfide synthesis. Many synthetic approaches to episulfides from epoxides, dihalides or chlorohydrins are known[1], but synthesis from olefins has not been studied much. Although direct episulfidation of olefins by photochemical reactions with carbonyl sulfide[2] or thioisocyanate[3] has been reported, the reactions do not seem to be suitable for synthetic utility. The recently reported two step synthesis of episulfides from olefins and sulfur monochloride[4] is an excellent procedure. However, easy disproportionation of sulfur monochloride to dichloromono- and polysulfanes results in the formation of β-chloroalkyl monosulfide, which cannot be converted into episulfide, as a by-product in the addition stage.

It was demonstrated that the reactions of anisole with substituted benzenethiosulfenyl chlorides in the presence of a trace amount of iron powder give disulfide or monosulfide depending on whether or not they have ortho nitro group[5]. The thiosulfenyl chlorides are monofunctional reagents protecting one of the chlorine atoms of sulfur monochloride with aryl groups and have the structure of sulfur appendage of the corresponding sulfenyl chlorides. They decompose gradually at room temperature to give the corresponding sulfenyl chlorides accompanied by the elimination of a sulfur atom. It might be possible to utilize this desulfuration character of thiosulfenyl chlorides for sulfur transfer reagents. Thus, the episulfidation reaction of olefins using the reagents was tried on the assumption that an episulfide can be directly obtained if a chloride anion in an intermediate, episulfonium salt, attacks the arylthio group to eliminate sulfenyl chloride.



Arenethiosulfenyl chlorides can easily be prepared from the corresponding thiophenols with sulfur dichloride in quantitative yields by the modified method for the preparation of known o-nitrobenzenethiosulfenyl or benzenethiosulfenyl chlorides[6]. They can be distinguished from the corresponding sulfenyl chlorides by nmr spectra[7]. The reaction of p-toluenethiosulfenyl chloride with cyclohexene at -78°C did not give the expected episulfide but a disulfide adduct quantitatively[8]. However, the crude disulfide adduct was easily converted into cyclohexene episulfide in 47 % yield by treatment with sodium amide at 80-90°C under reduced pressure. p-Tolyl disulfide was simultaneously obtained. Similarly, o-nitrobenzenethiosulfenyl chloride also gave the episulfide in a yield of 70 % from cyclohexene by treatment of the disulfide adduct with sodium amide. During the treatment we noticed the smell of amine which suggests the generation of hydrazine. Episulfidation was also successful by the use of sodium sulfide, which has been employed in the episulfidation of olefin-sulfur monochloride adduct[4], instead of sodium amide. An advantage of the use of thiosulfenyl chlorides in the synthesis of cyclohexene episulfide from cyclohexene is indicated in Table. Compared with the data using sulfur monochloride, the data for

Table Yields of Cyclohexene Episulfide[a,b]



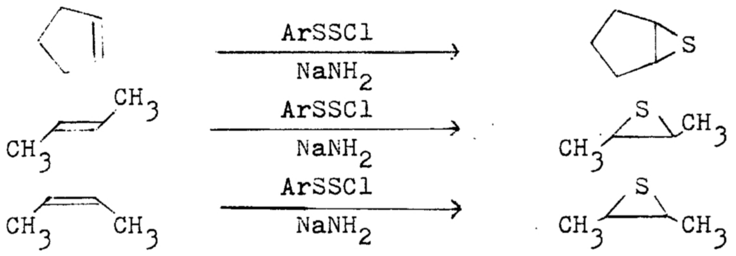
Reagent	p-$CH_3C_6H_4SSCl$	o-$NO_2C_6H_4SSCl$	S_2Cl_2
$NaNH_2$	47 %	70 %	15 %
Na_2S	77 %	72 %	33 %

[a] Isolated yield based on arenethiosulfenyl chloride or sulfur monochloride used.

[b] No attempt was made to optimize reaction conditions.

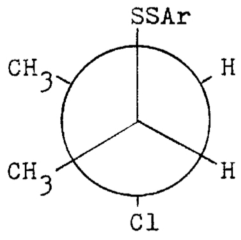
these thiosulfenyl chlorides show better yields of the corresponding episulfide.

Some representative examples of episulfides which were readily prepared with the use of thiosulfenyl chlorides and sodium amide are as follows: Cyclopentene episulfide, which is difficult to prepare from the corresponding epoxide since it proceeds through a cyclic intermediate such as thioxolane ring[9], was also obtained in 54-5 % yield from cyclopentene. Episulfidation of olefins by this procedure is stereospecific, since trans- and cis-2-butenes lead exclusively to the corresponding trans and cis episulfides respectively in 40-60 % yield, which showed exactly identical spectra with those of authentic samples[10].

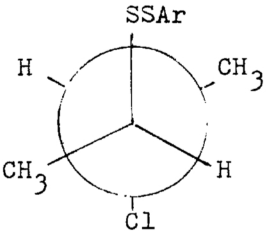


Ar = p-$CH_3C_6H_4$
or o-$NO_2C_6H_4$

The addition stage executed a key step for the stereospecificity of the new episulfide synthesis. Different patterns were observed in the nmr spectra of the addition products of cis- and trans-2-butenes[11]. Two methine protons in the adduct of I obtained from cis-butene and p-toluenethiosulfenyl chloride appear in the spectrum as ABX$_3$ octet (J_{CH_3-H} = 6.6 and J_{H-H} = 3.2 Hz). On the other hand, those in the adduct of II obtained from trans-butene show ABX$_3$ broad quintet (J_{CH_3-H} = 6.6 and J_{H-H} = 6.4 Hz).



I

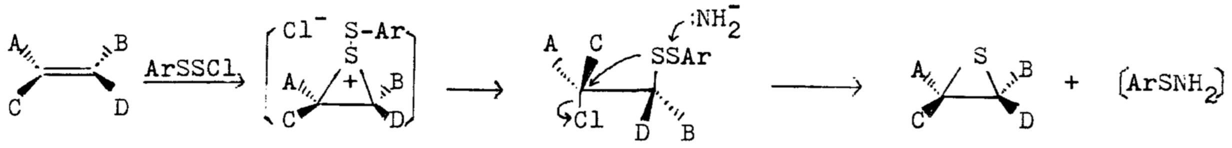


II

Ar = p-$CH_3C_6H_4$

These spectra suggest trans addition, in combination with the data in the addition of sulfenyl chlorides[12]. Thus the result shows that the episulfidation proceeds by trans addition through episulfonium salt as an intermediate[13] and by trans elimination with an attack of amide anion to arylthio group[14]. The arenesulfenamides formed are considered to undergo disproportionation immediately to aryl disulfides and hydrazine.

An important feature in the new episulfide synthesis is that a selection of substituted arenethiosulfenyl chlorides can be made. o-Nitrobenzenethiosulfenyl



$$2\,[\mathrm{ArSNH_2}] \longrightarrow \mathrm{ArSSAr} + [\mathrm{NH_2NH_2}]$$

chloride gives disulfide adducts quantitatively on treatment with olefins, but the reactivity is small because of the stabilization by ortho effect of nitro group[5]. On the other hand, p-tolyl derivative has such a high reactivity that it gives monosulfide adduct in a few cases such as the reaction with less reactive olefin as propylene. Thus, the yields of episulfides would be increased by the choice of thiosulfenyl chlorides and elimination conditions. This method of episulfidation using arenethiosulfenyl chlorides seems to be utilized widely and is particularly suited for the synthesis of episulfides from cyclic olefins.

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11 The chemical shifts of disulfide (I) from cis-butene appear at δ 4.29 due to the proton on sulfur attached carbon, at 3.17 due to that on chloro carbon and 1.27 due to that of methyl groups. Those of disulfide (II) from trans-butene appear at δ 4.10, 2.88, 1.58 and 1.37.

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13 Analogous addition of sulfenyl chloride or sulfur chlorides to unsaturated compounds is known to proceed via episulfonium salt; cf. ref. 11 and 4.

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