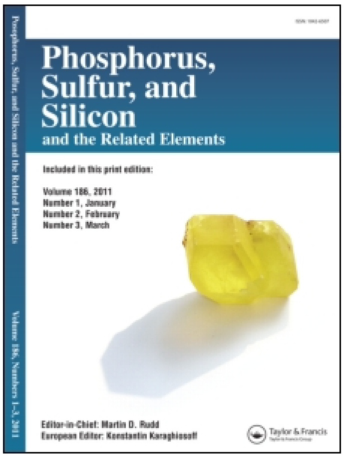

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Olefin Metathesis: A New Tool in the Synthesis of Organic Sulfur Compounds

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OLEFIN METATHESIS: A NEW TOOL IN THE SYNTHESIS OF ORGANIC SULFUR COMPOUNDS

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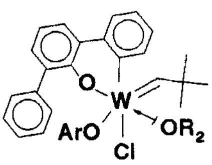
Abstract The metathesis of acyclic or cyclic olefinic sulfides is successfully achieved by using a chloro-aryloxide neopentylidene complex of tungsten as catalyst. This reaction constitutes a new route to the synthesis of various olefins, dienes or unsaturated polymers containing one or more S atoms.

The application of olefin metathesis to acyclic or cyclic olefins bearing functional groups offers many interesting possibilities for the synthesis of valuable organic products or polymers.[1,2] To date, the metathesis reaction has been applied to olefins containing O, N, halogen, or Si heteroatoms. We report here results that show that olefin metathesis can also be successfully applied to sulfur containing olefins by using the well-defined carbene homogeneous catalyst **1** we have recently synthesized.[3]

In the presence of **1**, the self-metathesis of allyl-methyl-sulfide depicted in scheme 1 leads to ethylene and to the di-sulfide olefinic compound in 20% yield.



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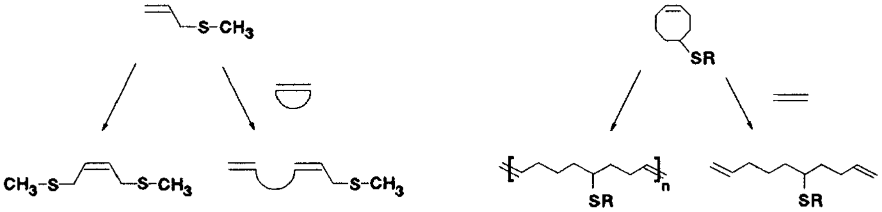


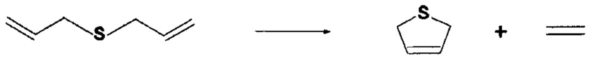
SCHEME 1 Some metathesis reactions of sulfur olefins.

More interestingly, by co-metathesis with an excess of 2-butene, allyl-methyl-sulfide gives crotyl-methyl-sulfide in 95% yield. Co-metathesis of allyl-methyl-sulfide with cyclopentene or norbornene leads to the associated sulfur dienes (scheme 1).

Ring-opening metathesis polymerization of various 5-alkyl-thio-cyclooctenes[4] (R = Et, *n*-Bu, *t*-Bu, *n*-Hex, *c*-Hex) (scheme 1) leads quantitatively to the corresponding sulfur polymers, with turnover rates higher than those observed in the metathesis of allyl-methyl-sulfide. For example, in the presence of **1** at 80°C, the quantitative polymerization of 500 equivalents of 5-*t*-Bu-thio-cyclooctene is completed in 30 min.

Reaction of *n*-butyl-thio-cyclooctene with an excess of ethylene in the presence of **1** gives a sulfur α,ω-diene (scheme 1) (75 % yield).

Finally, it was found that metathesis of allyl-sulfide leads, via an intramolecular cyclization process, to ethylene and to 2,5-dihydrothiophene (80-90% yield) (scheme 2). This last reaction opens a new route to thiophene synthesis starting from readily available products and indicates the potential of olefin metathesis in sulfur chemistry.



SCHEME 2 Metathesis of allyl-sulfide.

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