

Se-Phenyl *p*-tolueneselenosulfonate¹

Thomas G. Back, University of Calgary, AB, Canada
 Jeremy E. Wulff, University of Calgary, AB, Canada

Encyclopedia of Reagents for Organic Synthesis

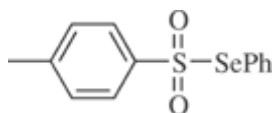
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Abstract



[68819-94-3] C₁₃H₁₂O₂SSe (MW 311.28)

Physical Data: mp 79.5–80 °C.

Solubility: soluble in chloroform, dichloromethane, THF, and benzene.

Form Supplied in: yellow, crystalline, odorless solid.

Preparative Methods: add *p*-toluenesulfonylhydrazide in methanol dropwise to an equimolar amount of benzeneseleninic acid in methanol at 0 °C; cool at –5 °C overnight, filter the highly pure crystalline selenosulfonate (96% yield);² alternatively, use 2 equiv of *p*-toluenesulfinic acid³ instead of *p*-toluenesulfonylhydrazide; several other preparative methods are also available;⁴ *Se*-phenyl benzeneselenosulfonate can be prepared in the same way and can be used similarly for most purposes.

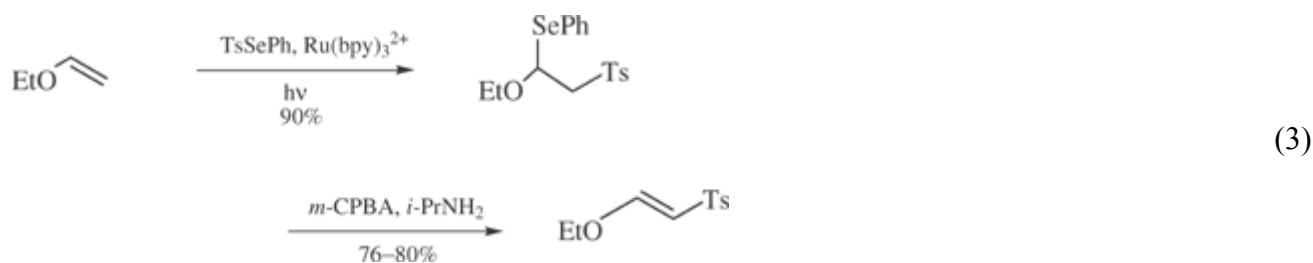
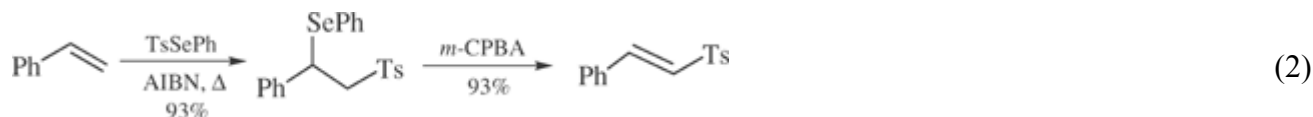
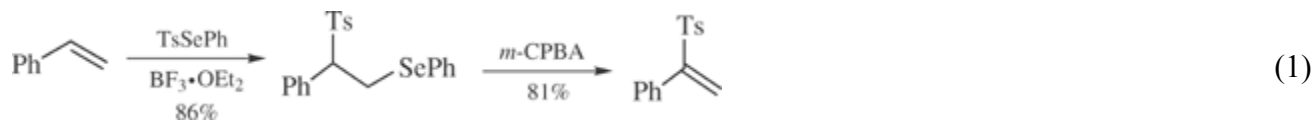
Purification: recrystallization from methanol (unnecessary when prepared as recommended above).

Handling, Storage, and Precautions: routine handling is possible, but avoid prolonged exposure to light and heat; store in the dark at 0 °C; may be toxic; use in a fume hood and avoid skin contact.

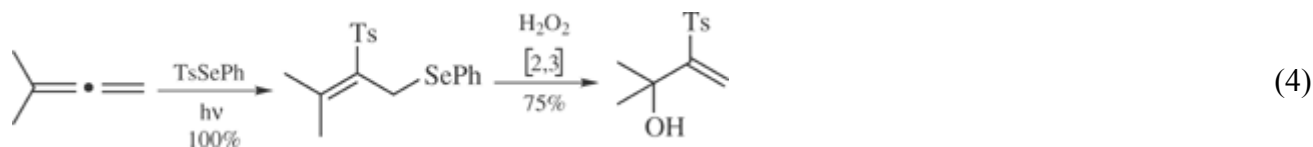
Selenosulfonation of Alkenes, Allenes, and Dienes

The 1,2-additions of the selenosulfonate to unsaturated substrates are known as selenosulfonations.⁵ Alkenes react under either Lewis-acid-catalyzed (eq 1) or free-radical conditions (eq 2). The former reactions proceed stereospecifically (anti) and regioselectively (Markovnikov),⁵ whereas the latter are nonstereospecific chain processes and afford the opposite regiochemistry (anti-Markovnikov).^{3,5} Free-radical additions may be initiated photochemically^{3,6} or by heating with AIBN⁵ in solvents such as benzene, chloroform or carbon tetrachloride. A ruthenium(II)-mediated photoaddition has been reported to be especially useful for electron-rich alkenes (eq 3).⁷ Selenoxide *syn*-elimination of the adducts can be effected with *m*-CPBA or hydrogen peroxide, affording high yields of the corresponding vinyl sulfones,^{3,5,6} which were in turn investigated as dienophiles in various Diels–Alder reactions.⁸ Applications have been reported in the synthesis of sterpuric acid^{8b} and hirsutene.^{8c} A

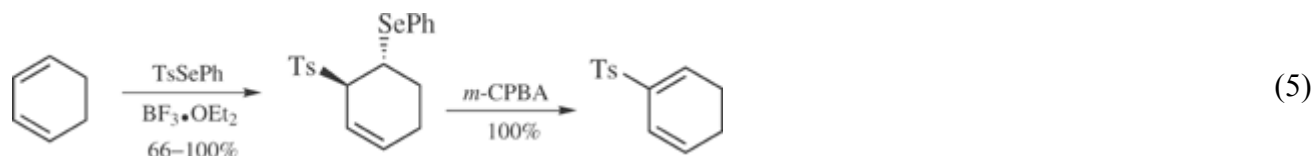
polystyrene-supported version of the selenosulfonate, attached to the polymer via the selenium moiety, has also been used in both the Lewis-acid-catalyzed and thermally initiated selenosulfonation protocols.⁹



Allenes undergo free-radical selenosulfonation with regioselective incorporation of the sulfonyl moiety at the central allenic carbon atom, producing 2-sulfonyl allylic alcohols after oxidation and [2,3] sigmatropic rearrangement of the corresponding selenoxides (eq 4).¹⁰

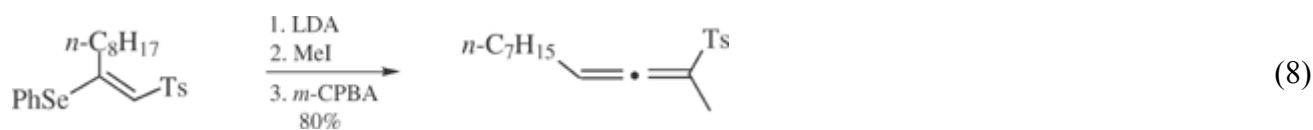
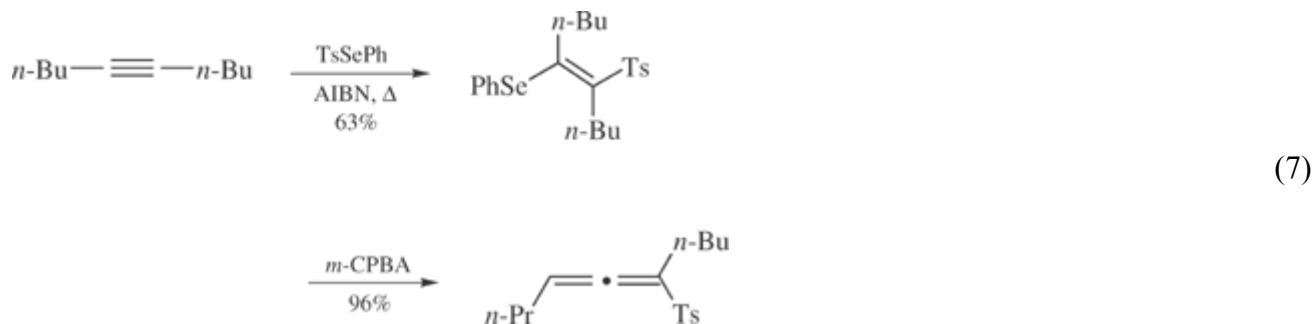
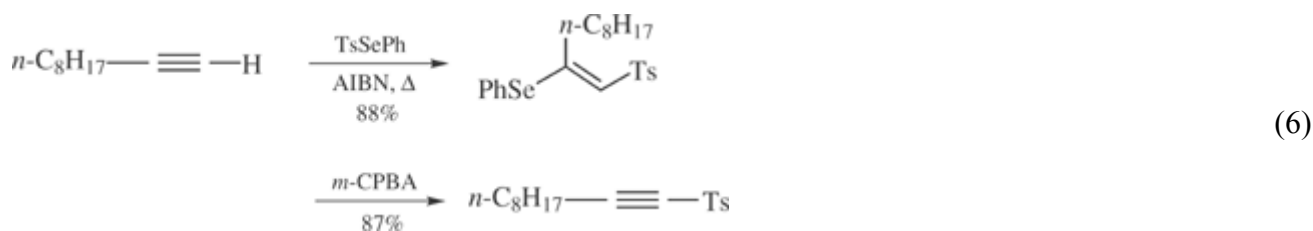


Conjugated dienes react with the selenosulfonate in the presence of boron trifluoride etherate to afford the corresponding 1,2-adducts, which produce 2-sulfonyl-1,3-dienes after selenoxide elimination (eq 5).^{5, 11} Cycloheptatriene produced the corresponding 2-sulfonylcycloheptatriene derivative in 57% overall yield upon similar selenosulfonation and selenoxide elimination.¹²

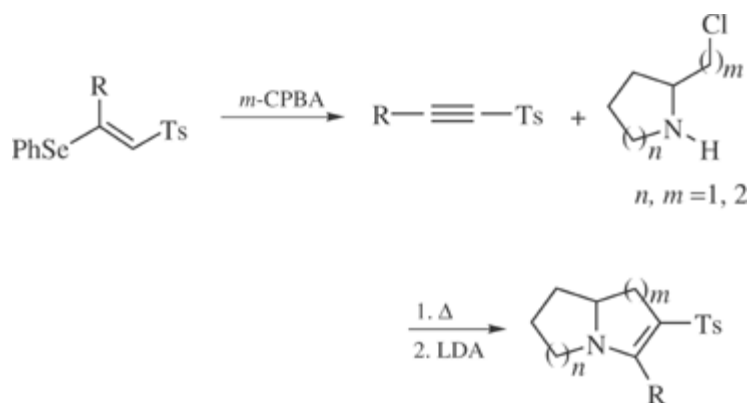


Selenosulfonation of Alkynes and Enynes

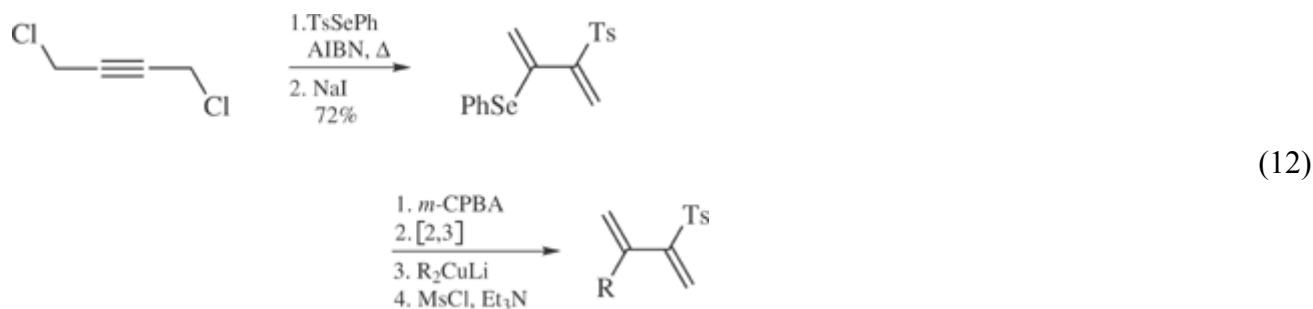
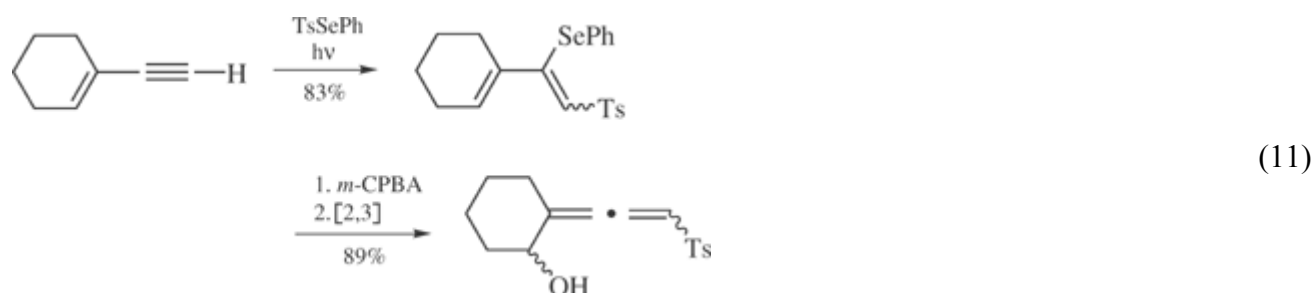
The free-radical selenosulfonation of alkynes proceeds via anti addition with anti-Markovnikov regiochemistry. Subsequent selenoxide eliminations produce acetylenic and allenic sulfones from terminal and internal alkynes, respectively (eqs 6 and 7).¹³ The 1,2-adducts can also be γ -deprotonated and alkylated in the α -position, resulting in the formation of the corresponding allylic sulfones. Selenoxide elimination of the latter compounds thus provides access to substituted allenic sulfones from terminal alkynes (eq 8).¹⁴ An enantioselective variation of this process based on asymmetric selenoxide eliminations in the last step has been reported.¹⁵ The 1,2-adducts or their selenoxides react with nucleophiles by addition-elimination or elimination-addition processes to give the products of overall substitution of the selenium residue (eq 9). Possible nucleophiles include organocuprates, alcohols, amines, cyanide, active methylene compounds, lithiated dithianes, and propargylic anions.^{13a,16} These protocols have been applied to the synthesis of the side chains of marine sterols¹⁷ and brassinosteroids.¹⁸ Acetylenic sulfones obtained via selenosulfonation react with amines containing pendant chloroalkyl or ester substituents to form various nitrogen heterocycles (eq 10), which have in turn been converted into dendrobatid alkaloids and related products.¹⁹



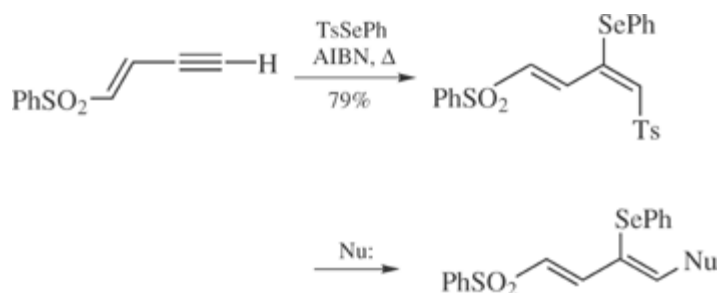
(10)



Enynes with terminal alkyne moieties cleanly afford the products of 1,2-addition to the triple bond (eq 11), but more highly substituted derivatives and those containing terminal alkene groups give more complex mixtures containing the products of addition to the double bond, as well as 1,4-adducts. Products such as the example in eq 11 afford allenic alcohols after oxidation and [2,3]sigmatropic rearrangement.²⁰ The selenosulfonation of 1,4-dichloro-2-butyne can be followed by reductive dehalogenation to afford the corresponding 2,3-adduct, thereby regenerating a unit of unsaturation and making the starting material function as an enyne equivalent. The 2,3-adduct can then be converted into various 3-substituted 2-sulfonyl-1,3-dienes as shown in eq 12.²⁰ The selenosulfonation of 1-sulfonylenynes affords adducts that undergo substitutions with Grignard reagents or heteroatom nucleophiles, as shown in eq 13.²¹

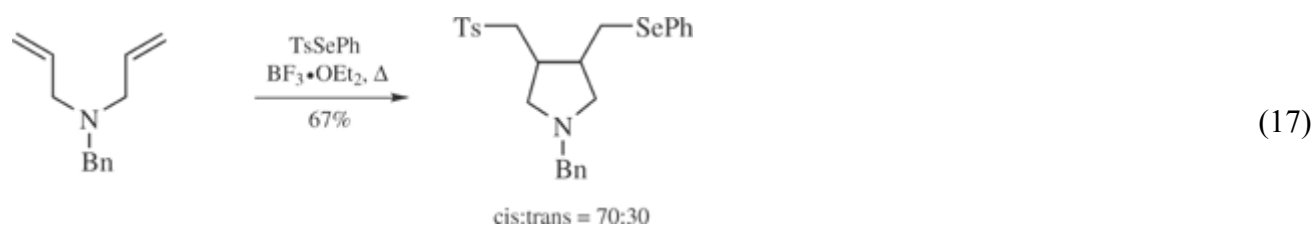
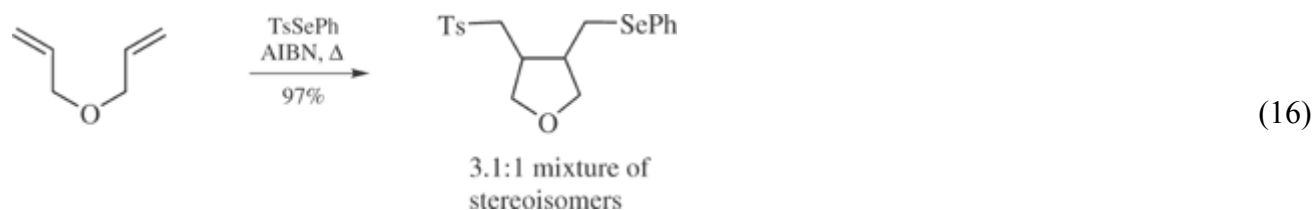
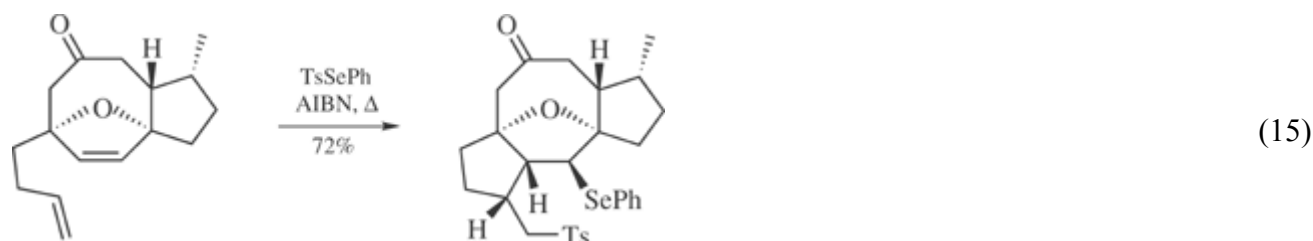
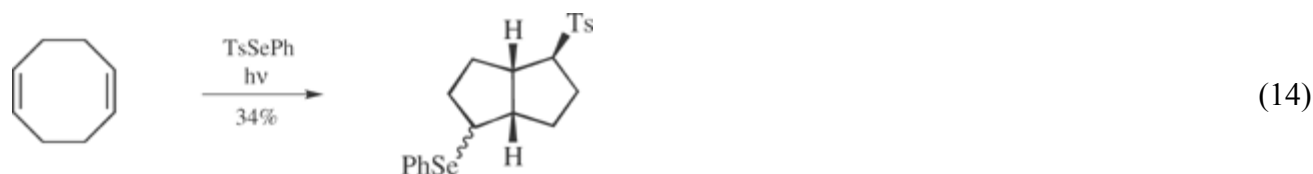


(13)

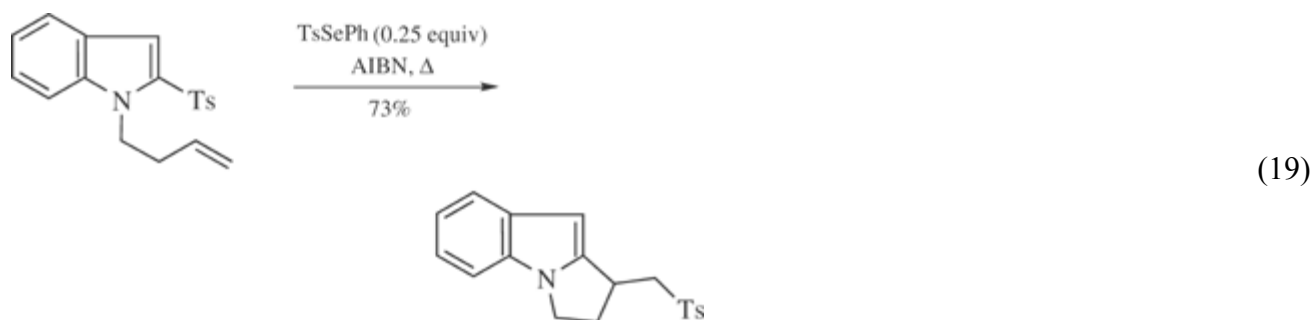
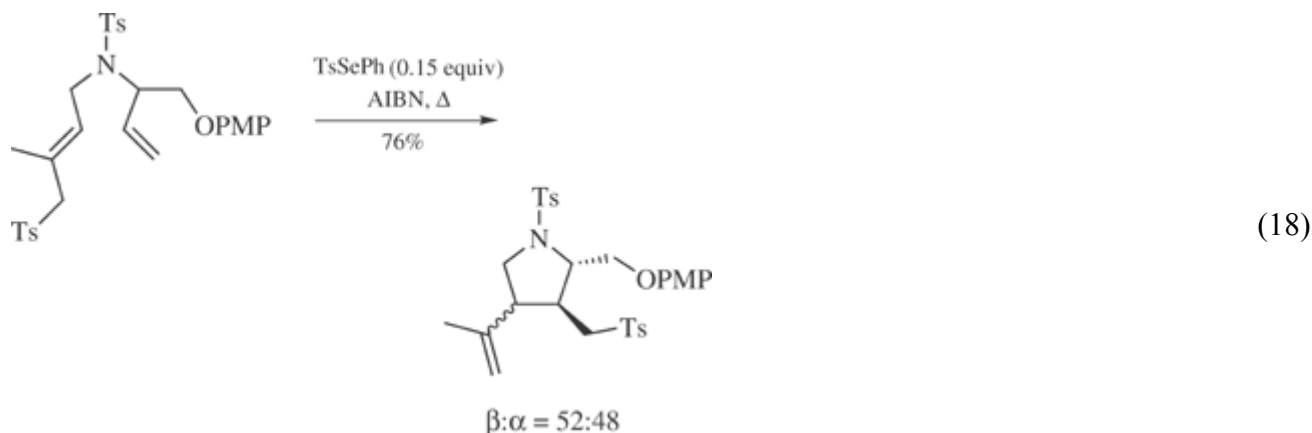


Radical Cyclizations

Several examples of radical cyclizations have been reported during the selenosulfonation of cyclic³ or acyclic dienes.²² When the tether linking the two alkene moieties includes a heteroatom, the procedure affords the corresponding heterocycles.^{22b,22c,22f} Illustrative examples are shown in eqs 14-17.^{3,22d,22b,22f} In eq 17, quaternization of the nitrogen atom with a Lewis acid affects the yield and stereochemistry of the radical cyclization. Similar cyclizations occur when unconjugated enynes^{22c} or bisallenes²³ are subjected to selenosulfonation.



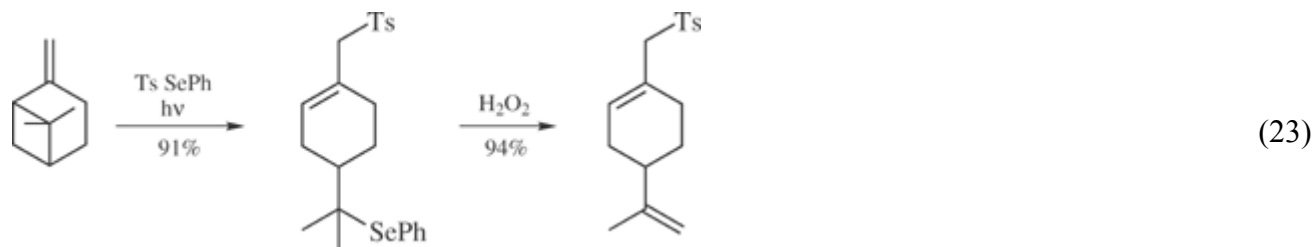
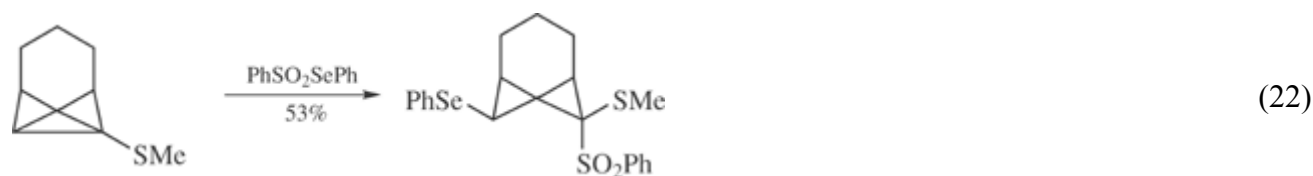
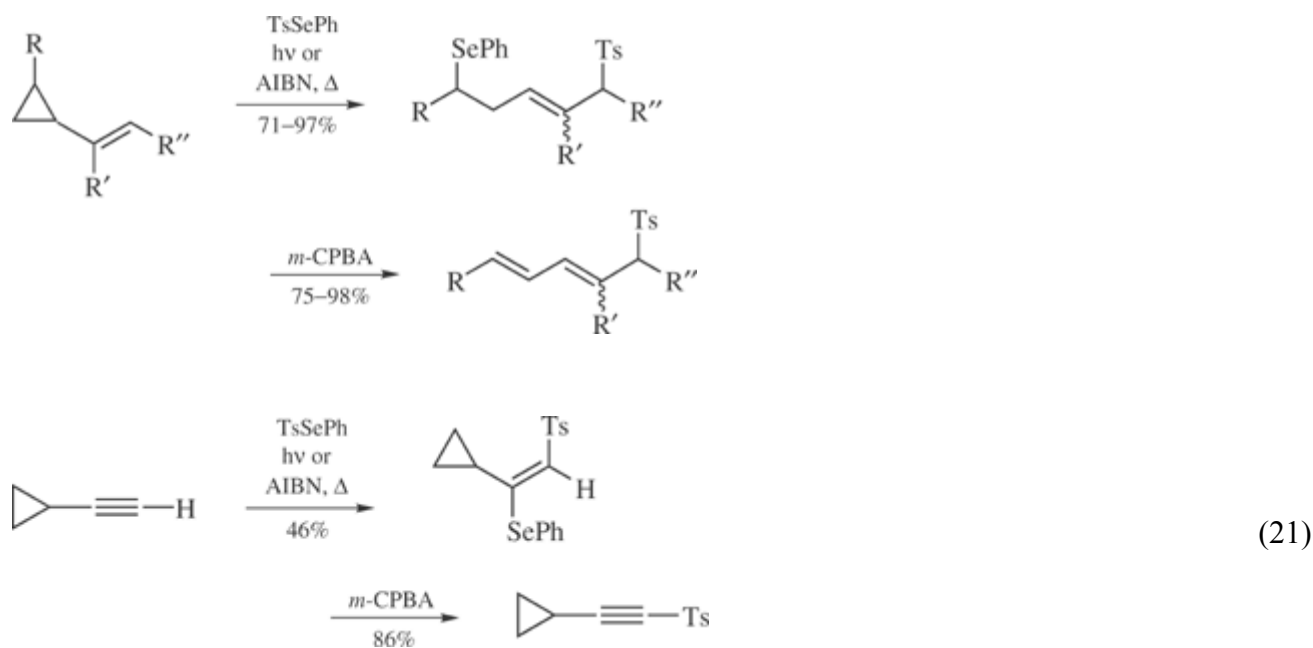
When one of the alkene units of the diene is replaced by an allyl sulfone moiety, cyclization may be initiated with a smaller than stoichiometric amount of the selenosulfonate, since displacement of a sulfonyl radical from the allyl sulfone group propagates the chain reaction (eq 18).^{22f,24} A related procedure that leads to the cyclization of sulfonyl-substituted indoles is shown in eq 19.²⁵



Selenosulfonation of Compounds with Small Rings

The free-radical selenosulfonation of vinylcyclopropanes is accompanied by ring-opening to give 1,5-addition products that afford 1-sulfonyl-2,4-dienes by selenoxide elimination (eq 20).²⁶ Similar ring-opening is observed in cyclopropylidenes, whereas cyclopropylacetylene undergoes mainly 1,2-addition and provides the corresponding acetylenic sulfone after selenoxide elimination (eq 21).²⁶ The tricyclo[4.1.0.0^{2,7}]heptane in eq 22 underwent ring-opening even at room temperature,²⁷ while β -pinene was similarly cleaved under photochemical conditions (eq 23).^{22a}

(20)



Miscellaneous Reactions

The reactions of the selenosulfonate with acyl derivatives of *N*-hydroxy-2-thiopyridone,²⁸ alkyl, alkenyl, and alkynyl derivatives of tin and mercury;²⁹ triethylgermane³⁰ and diazomethane³¹ have also been reported, but the synthetic potential of these processes remains to be determined.

Related Reagents

[Benzeneselenenyl Bromide](#); [Benzeneselenenyl Chloride](#); [Benzeneselenenyl Trifluoromethanesulfonate](#); [Diphenyl Diselenide](#); [N-Phenylselenophthalimide](#); *Se*-phenyl trifluoromethaneselenosulfonate.

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