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Oxidative addition of trifluoromethanesulfonamide to cycloalkadienes

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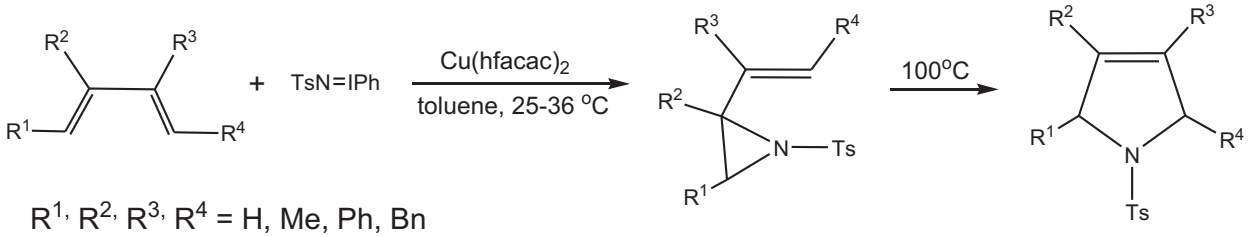
ABSTRACT

In the oxidative system (*t*-BuOCl+NaI) trifluoromethanesulfonamide is regio- and stereoselectively added to only one double bond of cyclopentadiene and 1,3-cyclohexadiene giving rise to 1,1,1-trifluoro-*N*-(5-iodocyclopent-2-en-1-yl)methanesulfonamide **7** and *trans*-*N*,*N*′-cyclohex-3-en-1,2-diylbis(1,1,1-trifluoromethanesulfonamide) **8**. The structure of **7** and **8** was determined by X-ray, NMR, and MS. With 1,4-cyclohexadiene, addition to both double bonds occurs with the formation of *N*,*N*′-(4-chloro-5-iodocyclohexan-1,2-diyl)bis(1,1,1-trifluoromethanesulfonamide) **9**. Under the action of sodium iodide in acetone, the latter product undergoes halogenophilic attack with the reduction of the CHI group and elimination of HCl to give *trans*-*N*,*N*′-cyclohex-4-en-1,2-diylbis(1,1,1-trifluoromethanesulfonamide) **10**, whose structure was also determined by X-ray analysis. 1,3,5-Cycloheptatriene under these conditions is oxidized to benzaldehyde and does not react with trifluoromethanesulfonamide.

1. Introduction

In continuation of our studies of the reactions of trifluoromethanesulfonamide (triflamide) with compounds having one or two C=C bonds under oxidative conditions,[1–4] in the present work we report on the reactions of triflamide **1** with cyclopentadiene **2**, 1,3-cyclohexadiene **3**, 1,4-cyclohexadiene **4**, 1,3,5-cycloheptatriene **5**, and 1,3-cyclooctadiene **6** in the oxidative system (*t*-BuOCl+NaI). Except for our recent work on the formation of 9-heterobicyclo[4.2.1]nonanes in the reaction of triflamide with 1,5-cyclooctadiene,[4] there are no data in the literature on the reactions of sulfonamides with dienes in oxidative systems, that is, under conditions in which the corresponding sulfonylnitrenes can be generated. At the same time, both linear and cyclic 1,3-dienes react with *N*-tosylphenyliodinane PhI=NTs, as a source of tosylnitrene to form aziridines by 1,2-addition to only one double bond of the diene.[5,6] Only two examples of 1,4-addition of the thus generated sulfonylnitrenes to 1,3-dienes were reported: the reaction of TsN=IPh with 1,3-cyclooctadiene giving rise to 9-(*p*-tosyl)-9-aza-bicyclo[4.2.1]non-7-ene[5] and the reaction of RN=IPh (R=Ts, Ns) with acyclic 1,3-dienes and 1,3-cyclooctadiene in the presence of copper 1,1,1,5,5,5-hexafluoroacetylacetonate Cu(hfacac)$_2$ leading to 3-pyrrolines.[7] The latter reaction, however, only formally can be considered as 1,4-addition (or [1+4]-cycloaddition) since it was shown that at room temperature or moderate heating to 36 °C 2-vinylaziridines were formed, which underwent isomerization to 3-pyrrolines only upon further heating to 100 °C.[7]



Similarly, 1,3-cyclooctadiene with RN=IPh (R=Ts, Ns) at 100 °C gives vinylaziridines, which rearrange to the corresponding 9-aza-bicyclo[4.2.1]non-7-enes only upon heating to 150 °C.[7]

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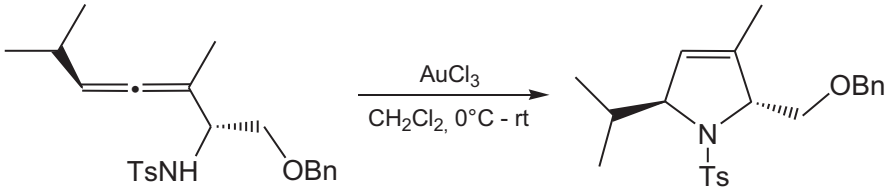
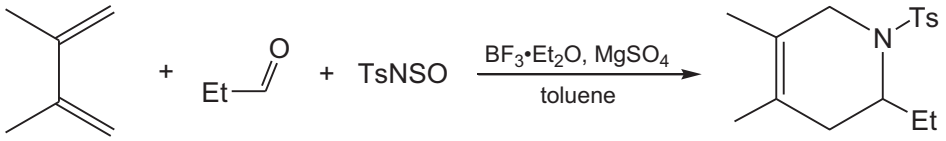
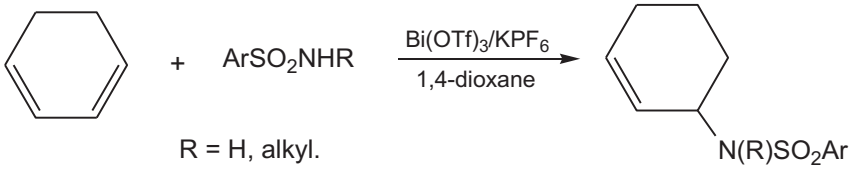
Apart from the products of heterocyclization, the reactions of 1,3-dienes with sulfonamides may result in the formation of monoadducts having the intact C=C double bond at the 3 position with respect to the entering sulfonamide group, or *N*-allylsulfonamides. The latter compounds are valuable intermediates in the synthesis of heterocycles, allylamines, and amino acids; therefore, it seems reasonable to summarize briefly the existing methods of assembling the *N*-allylsulfonamide fragment. Thus, 3-pyrrolines are also formed by the $AuCl_3$-catalyzed intramolecular cyclization of α-tosylamidoallenes.[8]



N-Tosyltetrahydropyridine having the endocyclic allylsulfonamido moiety, which is the six-membered analog of the above 3-pyrroline products, was obtained by the hetero-Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene with *N*-propylidenetosylamide formed in situ from *N*-sulfinyltosylamide and propanal.[9]

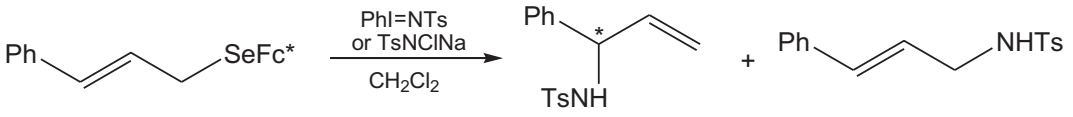


N-Allylsulfonamides with an exocyclic sulfonamide group and an endocyclic allyl group are formed by the bismuth triflate-catalyzed addition of arenesulfonamides to 1,3-cyclohexadiene.[10]



This reaction is also catalyzed by silver triflate, which was successfully employed also for hydroamination of other 1,3-dienes as well as alkenes.[11]

The reaction of PhI=NTs or TsNClNa with an allyl selenide having chiral substituted ferrocenyl residue affords a mixture of *N*-allyltosylamides with internal or terminal tosylamido group.[12]



Intramolecular cyclizations with the formation of an *N*-allylsulfonamide moiety are also known. Thus, the Au(I) complexes-catalyzed intramolecular cyclization of 5-(2-tosylaminoethyl) cyclohexa-1,3-diene proceeds upon heating to give 8-tosyl-8-azabicyclo[3.3.1]non-2-ene having an *N*-allylsulfonamide moiety.[13] Note, that room temperature $Pd(OAc)_2$-catalyzed reaction in acetic acid gives rise to 1-tosyl-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-yl acetate[14] (the formation of the intermediate compound with TsNH instead of AcO group cannot be ruled out).

A series of five- and six-membered *N*-allyltosylamides was obtained by the reaction of silyl enol ethers of the corresponding cycloalkanones with the Sharpless aminating reagent TsN=Se=NTs in low to moderate yield with retention of the silyl moiety.[15]

The Sharpless reagent was introduced into synthetic practice in the middle of 1970s and used for preparation of various *N*-allylsulfonamides by the reaction with alkenes.[16,17] The products of allylic sulfonamidation are formed also in the reaction of alkenes with *N*,*N*′-disodium bis(arenesulfonamido)selenium dichlorides $(ArSO_2NNa)_2SeCl_2$.[18] Finally, *N*-allylsulfonamides having two sulfonamido residues in the molecule were prepared by the reaction of cyclic dienes with the Sharpless reagent[19–22] or $(PhSO_2NNa)_2SeCl_2$.[18] The tosyl protecting group can be removed to prepare the corresponding diamines.[21,22]

1,2-Bis(tosylamido)alkenes are also formed by the ring reaction of the corresponding vinylaziridines with tosylamide in the presence of tetrabutylammonium fluoride in quantitative yield.[23]