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A FREE RADICAL ADDITION-CYCLIZATION REACTION OF 1,6-DIENES WITH SULFONYL CHLORIDE

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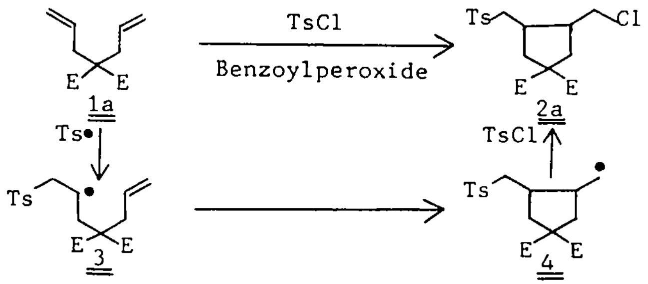
Summary: A free radical addition-cyclization reaction of 1,6-dienes with *p*-toluenesulfonyl chloride in the presence of benzoylperoxide giving cyclopentane systems is described.

Recently there has been a growing interest in the application of radical cyclization reaction in organic synthesis.[1,2] Free radical intramolecular C-C bond-forming reactions has been used in the preparation of various carbocyclic and heterocyclic systems.[3] The free radical addition-cyclization reaction of 1,6-dienes with thiyl and other radicals has been noted by several groups.[4] We have recently examined the feasibility of sulfonyl chlorides in free radical addition-cyclization reaction.[5] This report describes the results of free radical reaction of 1,6-dienes with *p*-toluenesulfonyl chloride.

1a (1.1mmol) was allowed to react with *p*-toluenesulfonyl chloride (11mmol) and benzoylperoxide (0.12mmol) in toluene (10mL) at 100°C for 7 h to produce 85% yield of 2a as a 6:1 mixture of *cis* and *trans* isomers.[6] We were not able to isolate any six-membered ring product. The generality of this reaction is illustrated on Table I.

A proposed mechanism for this free radical addition-cyclization reaction is outlined in Scheme I. Initiation occurs by *p*-toluenesulfonyl radical addition to diene 1a, followed by 5-exo cyclization and chlorine atom abstraction from *p*-toluenesulfonyl chloride to give 2a.

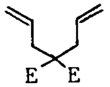
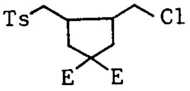
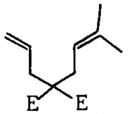
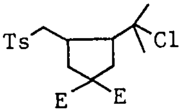
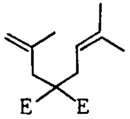
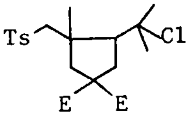
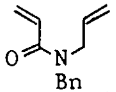
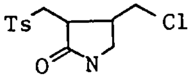
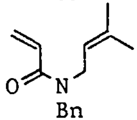
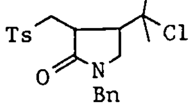
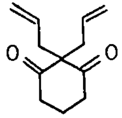
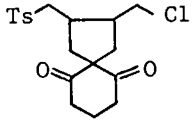
Scheme I



The relative stereochemistry of the isomeric products was determined by examining the relative ratios shown in Table I. Since the ratio of isomeric products decreases as the steric effect of the substituents increases, we believe that the major product should be *cis* isomer. This result is consistent with literature reports.[4]

In conclusion, the regio- and stereo- selectivity of this reaction demonstrates the potential of this strategy for the construction of functionalized five-membered ring systems.

Table I: The Free Radical Reaction of 1,6-Dienes

Entry	Substrate	Product	Yield (ratio)[6]
a			85% (6:1)
b			89% (3.3:1)
c			81% (1.4:1)
d			64% (4:1)
e			97% (1.9:1)
f			70% (5:1)

E: CO_2Me

Bn: $PhCH_2$

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6. Ratios refer to isomeric products and are based on HPLC analysis or isolated yields.

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