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Sodium *p*-Toluenesulfinate/Copper(II) Acetate In Free Radical Reactions

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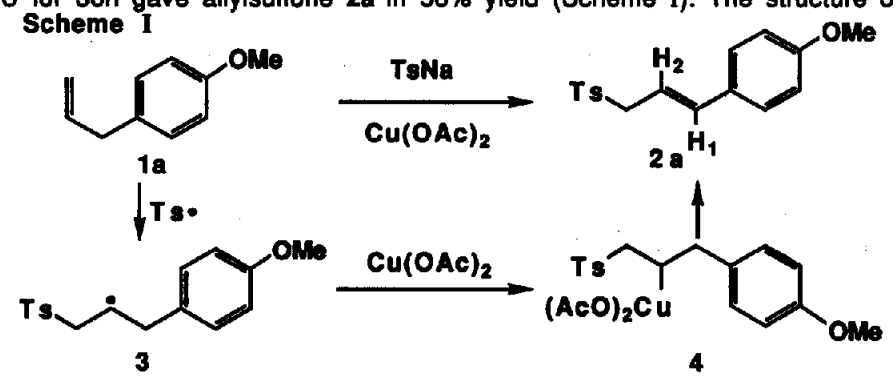
Key Words: Sodium *p*-toluenesulfinate/copper(II) acetate; Free radical reaction; Alkenes

Abstract: A free radical reaction of alkenes with sodium *p*-toluenesulfinate/copper(II) acetate to give *p*-toluenesulfonyl group substituted alkenes, cyclopentane and tetralin systems is described.

Recently there has been a growing interest in the application of radical reaction in organic synthesis.[1] Free radical reactions mediated by sulfonyl radical have been noted by several groups.[2,3] It has been reported that carbon radicals can be oxidized to alkenes by copper(II).[4,5,6] *p*-Toluenesulfonyl radical can be generated from sodium *p*-toluenesulfinate in aqueous acetic acid.[7] This report describes the results of free radical reaction of alkenes with sodium *p*-toluenesulfinate/copper(II) acetate.

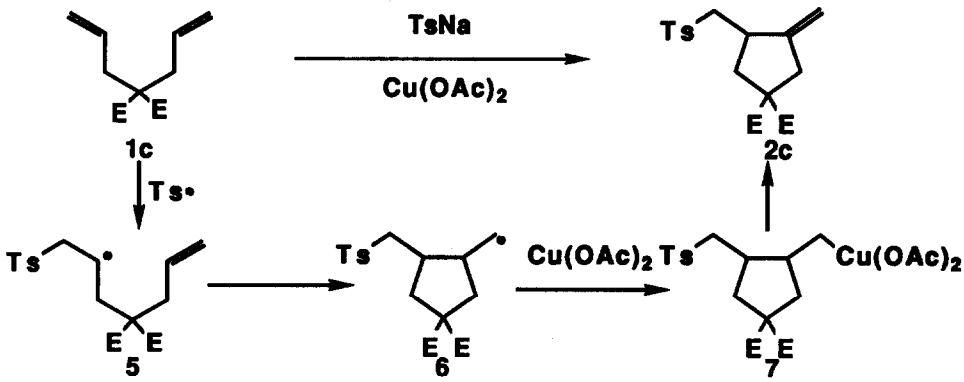
We began our studies by examining the reaction behavior of **1a**. Thus, treatment of **1a** with sodium *p*-toluenesulfinate/copper(II) acetate in aqueous acetic acid at 90°C for 36h gave allylsulfone **2a** in 56% yield (Scheme I). The structure of **2a** was

Scheme I



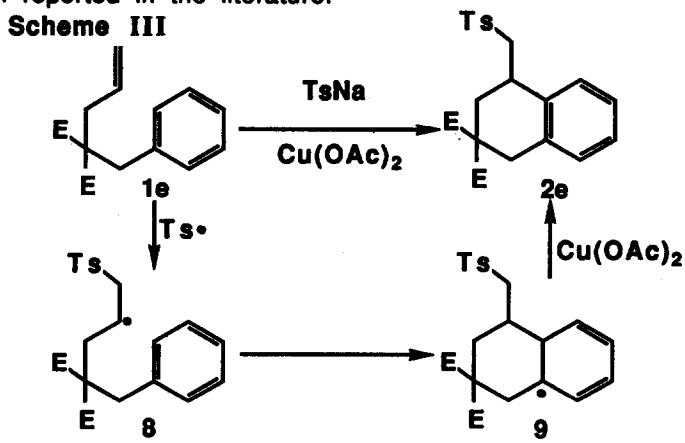
determined by ^{13}C and ^{1}H NMR (J_{H1-H2}=16Hz). This reaction presumably occurs via the addition of *p*-toluenesulfonyl radical to **1a**, followed by the oxidative elimination of radical intermediate **3**.

Scheme II



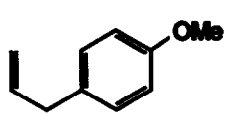
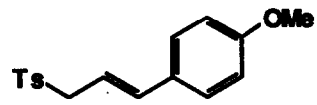
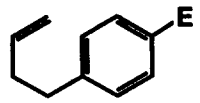
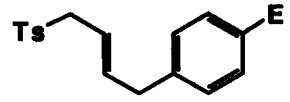
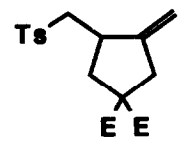
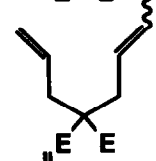
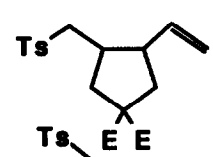
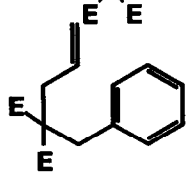
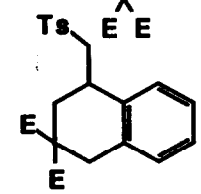
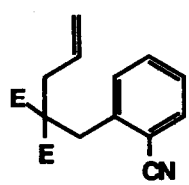
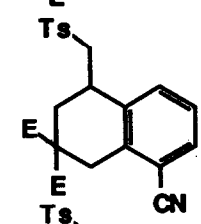
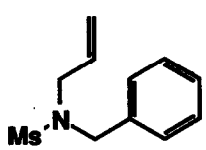
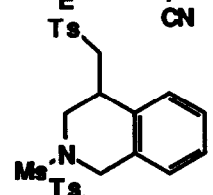
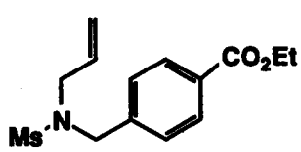
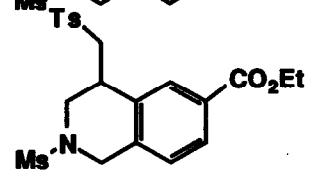
The addition reactions of sulfonyl radical to 1,6-dienes have been reported by several groups.[3,7b,7c,7d] Based on the results shown in Table I (Entry a and b), we believe that the reaction of 1,6-diene with sodium *p*-toluenesulfinate/copper(II) acetate via the reaction pathway shown in Scheme II can be effective. Reaction of **1c** with sodium *p*-toluenesulfinate/copper(II) acetate in aqueous acetic acid at 90°C for 15h gave 51% of **2c** (Table I, Entry c). No six-membered ring product could be isolated. Similarly, free radical reaction of **1d** with sodium *p*-toluenesulfinate/ copper(II) acetate gave Hofmann elimination product **2d** in 73% yield (Table I, Entry d). The selective Hofmann oxidative elimination of carbon radical with copper(II) acetate has been reported in the literature.[6]

Scheme III



The oxidative cyclization of the carbon radical on to the aromatic ring offers an attractive route to tetralin derivatives.[5a,5d] Reaction of **1e** with sodium *p*-toluenesulfinate/copper(II) acetate in aqueous acetic acid at 90°C for 60h gave 72%

Table I: Sodium *p*-Toluenesulfinate/Copper(II) Acetate in Free Radical Reactions

Entry	Substrate 1	Mole Equiv. TsNa	Mole Equiv. $Cu(OAc)_2$	Product 2	Yield
a		20	4		56%
b		20	4		54%
c		10	2		51%
d		10	2		73%
e		30	6		72%
f		20	4		82%
g		40	8		73%
h		30	6		68%

E: CO_2Me, Ms: $MeSO_2$

of **2e**. This free radical cyclization reaction most likely proceeded by the mechanism shown in Scheme III.

These results demonstrate that this sodium *p*-toluenesulfinate/copper(II) acetate reaction provides a route to *p*-toluenesulfonyl group substituted alkenes, cyclopentane, tetralin systems. Further work on the methodology is in progress.

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